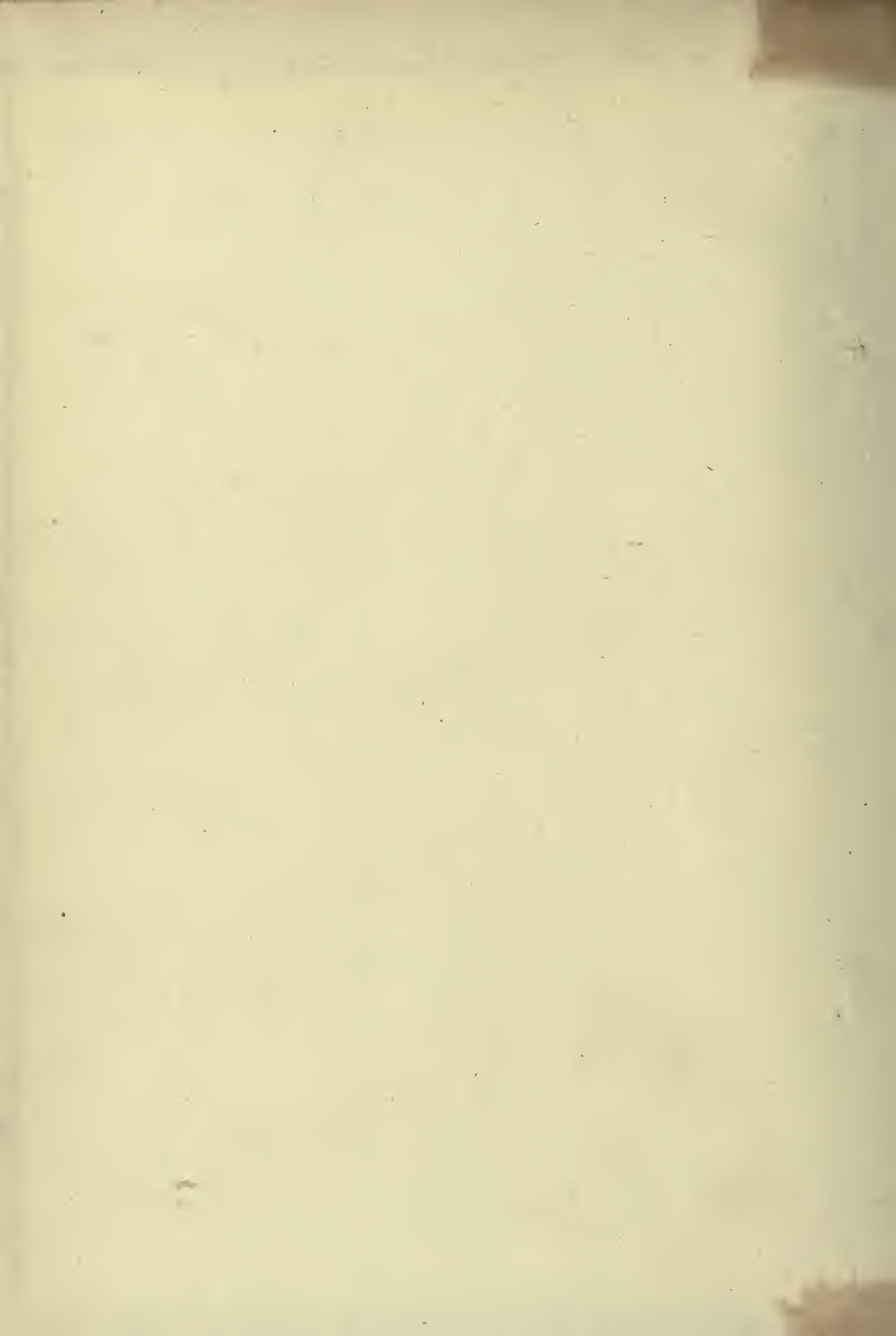






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ON THE DETERMINATION OF THE MELTING POINTS OF MINERALS.*

PART I.—THE USES OF THE MELDOMETER.

By J. JOLY, M.A., B.E., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

THERE appears to have been no serious attempt made in recent times by mineralogists to effect the determination of the melting points of minerals with a degree of accuracy in keeping with our present means of measuring high temperatures. Nor has there been any suggestion, to the best of my knowledge, as to the possibility of providing a simple and accurate means of observation. The present paper (preliminary to one embodying the melting points of the more abundant mineral species) is occupied with an account of a method of effecting such determinations which it is hoped possesses qualities of simplicity and accuracy. It will be seen that its use necessitates only the most minute quantities of the substance, and hence the method is applicable for dealing with rare mineral species or small quantities of chemically prepared bodies; other applications of the method besides the determination of melting points are suggested in this paper. In meeting the expenses connected with the development of the apparatus, I have to acknowledge thankfully a grant made to me by the Royal Irish Academy.

The scale of fusibility of Van Kobell is still quoted in the most recently published mineralogical works. It constitutes a comparative method, beset with errors, even as a means of identification, save under special circumstances. Thus whether a splinter of a mineral will melt in the flame of the blowpipe depends as much, or more, on the shape, conductivity, and dimensions of the splinter as on its melting point. For example, a filament of the fibrous actinolite is more easily fused than a fragment of the compact orthoclase. The melting point of actinolite is, however, some 100° Centigrade above that of orthoclase. Again, the chemical action of the flame may sometimes interfere. But not alone do these sources of error arise in comparing the behaviour of substances in the blowpipe flame, but the scale of Van Kobell is itself highly irregular in its spacing, and even erroneous in the order of fusibilities. Thus the melting and softening points in Centigrade degrees of specimens of Van Kobell's standards, as determined by the method to be described later, are as follows :—

	Melting. ° C.	Softening. ° C.
1. Stibnite	525 ..	—
2. Natrolite	965 ..	—
3. Almandine	1265 ..	972
4. Actinolite (green) ..	1296 ..	971
5. Orthoclase	1175 ..	865
6. Bronzite (Diallage) ..	1300 ..	—
7. Quartz	1430 ..	—

The numbers prefixed give the order of fusibilities as ordinarily given for Van Kobell's scale. The wide difference observable between the temperatures at which softening may be first detected and those at which melting, in the ordinary sense of liquefaction, is attained, is due to the viscosity of the substances. Unfortunately, this property of viscosity appears, to a greater or less degree, common to the mineral silicates, and is most conspicuously displayed in the case of quartz itself. It is, of course, impossible to assign any quite definite melting or softening point in such cases, whatever the method of determination adopted. There is no sudden change of state. A fact well shown in the curve of the thermal capacity of melting basalt recently determined by Professors Austen and Rücker (*Phil. Mag.*, vol. 32, p. 353). Possibly the temperature corresponding to the upper bend of the curve when the latent absorption appears nearly or quite complete should, in accordance with the facts attending the liquefaction of non-viscous bodies, be defined as the melting temperature. A point apparently a little below 900° C. in the case of basalt. But the temperature is not well defined. In connection with what is said above as to the possible chemical effects of the blowpipe flame, it is interesting to notice further that Professors Austen and Rücker observe upon discrepancies introduced into their experiments, apparently traceable to the chemical action of the flame, whether reducing or oxidising, used in effecting the meltings.

From present experience, it appears as if the high degree of viscosity possessed by silica, where this body constitutes a considerable constituent of a substance, may have the effect of masking the influence on the melting point of small variations in the percentages, or in the nature, of the bases present. To what extent this will prove to be the case future experiments must decide. That it should be so at all is unfortunate for many purposes of determination. But it is at least certain that the melting or softening intervals of a viscous mineral substance may be rendered of far higher discriminative and scientific value than is attained by use of the blowpipe method of determination. In the case of non-viscous bodies, such as halite, stibnite, &c., a definite temperature or melting point is readily found by the method described in this paper. The terms "melting

* A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

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point" and "softening point," as applied to viscous bodies in this paper, are defined further on, as well as the mode in which they are determined.

The "Meldometer" ($\mu\epsilon\lambda\delta\omega$, I melt), as I have designated the instrument used in determinations of melting-points, is of the following construction:—A ribbon of pure platinum, having a width of about 1.2 m.m., is stretched between forceps, furnished each with a binding screw, and insulated from each other so that on connecting the binding screws with a battery a current can be passed through the ribbon. Upon the surface of this ribbon the substance to be examined is placed. It is necessary first to reduce the mineral to a fine powder in an agate mortar, and finally grind it with a little water till in the form of a fine fluent paste; a speck of this is spread over a small area of the ribbon. The best condition for observing melting is when a few particles are *thinly* spread here and there upon the platinum. A quantity invisible to the unassisted eye may be dealt with, for in all cases the phenomena of melting are observed through a microscope. The microscope having been brought to bear upon the *thin* coating of the powdered mineral upon the platinum, a current of gradually increasing intensity is passed through the ribbon till the mineral melts or volatilises. In this process the mineral often exhibits very characteristic phenomena. It remains to describe how the temperature of the platinum ribbon at the moment at which the mineral melts may be determined. Commencing, however, with the simplest form of the apparatus, I proceed to describe a form of the meldometer with which observations, *directly* comparative between the substance being investigated and other substances of known melting-points, are effected. In cases in which identification is the object in view, we compare the behaviour of the substance with that of the species to which we think it referable from its other characters.

Simple Form of the Meldometer.

Fig. 1 shows, to half real scale, a plan and side elevation of this form of the meldometer intended to rest on the stage of a microscope.* It consists of two forceps—one insulated—attached to a disk-shaped brass plate. This latter may be held down on the stage of the microscope by the stage clamps, and is placed so that the ribbon stretched between the forceps is brought to traverse the field of view. A one-inch foreign objective of cheap pattern is suitable for this work. I have had one in use for some years, and it seems uninjured. These powers have single lenses. If a compound cemented objective is used, the Canada balsam used in the cementing melts if observations be prolonged at the higher temperatures. The forceps holding the ribbon close by their elasticity, and are opened by the small screws threaded into the upper member of each forceps. The ribbon is shown cut away where it is held by the forceps. This is done with a scissors before inserting it. The object is to secure a more uniform temperature over the length of the ribbon, which otherwise diminishes rapidly in temperature approaching the forceps by reason of thermal conductivity, the effect being intensified by decreased electrical resistance where the ribbon is colder. The effect of reducing the section is to diminish this loss of heat by conduction, and at the same time the electrical resistance increasing with diminished cross section up to the forceps causes a development of heat which augments as the cold metal of the forceps is approached. In this way the loss of heat to the forceps is made good, and the central parts of the short strip made more uniform in temperature. Exact uniformity of temperature throughout is not needful, for the method is one of comparison, and if the substances being compared are brought to adjacent portions of the ribbon, it may be assumed they are under like conditions as regards temperature.

* This form has been already noticed briefly in *Nature*, xxxiii., 1885, pp. 15, 16. See also *Journ. Roy. Micro. Soc.*, x., p. 1068. A further notice of the meldometer is reported from a paper read before the British Association at Bath, 1888, in *Industries*, vi., p. 20.

The length assigned to the ribbon is conveniently about 2 c.m. A storage cell or a couple of Grove cells will furnish sufficient current to raise to a blinding white heat and finally fuse the ribbon. The current is regulated as follows:—Two rods of carbon, 51 c.m. in length, 17 m.m. in diameter, such as are used for electric-arc lighting, having each a resistance of about half an ohm, are clamped at their ends upon a piece of board. A sliding-piece consisting of two sprung brass tubes encircling each carbon, and connected by a cross-piece of brass, can be moved along from end to end of the carbons. At one end the carbons are each furnished with a binding screw, and are insulated from one another save where connected by the sliding-piece. This resistance is placed in circuit with battery and meldometer, so that the current flows through more or less of the carbon rods according to the position of the slider. Thus, the total resistance in circuit may be varied by moving the latter, and in this way the quantity of current traversing the circuit controlled. Having placed the two substances to be compared side by side, we can thus expose both to any temperature up to that at which the platinum breaks. It will be found that quartz may be melted before this point is reached, and reduced to a glass which no longer affects polarised light. At these high temperatures the

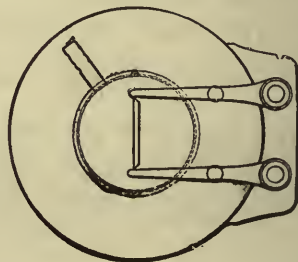


FIG. 1.

light is very intense, and it is necessary to shield the eye from its effects. A cover-glass smoked over a lamp flame may be placed above the eye-piece of the microscope, but a small piece of neutral tinted glass, such as is used in snow spectacles, is better for the purpose.

When the platinum is heated in this form of the meldometer, as the forceps are fixed in position, the expansion results in considerable sag of the ribbon. This, however, is only an inconvenience in so far as it necessitates re-focussing the microscope upon the object. By making one of the forceps free to rotate on a vertical axis at the binding screw, and affixing a weak, spiral controlling spring, so that the ribbon is always distended by a small force, this inconvenience may be avoided, or the distance of the forceps apart may be adjustable by a screw (see figure in the *Journ. Royal Micros. Society*, x., p. 1068); but the simpler form of the apparatus is preferable.

Employment of the Simple Meldometer.

If we seek to identify the body, of course we ultimately compare it with accredited specimens of the body we suspect it to be; and here, even if infusible below the melting-point of the platinum, information is often gained by comparing the behaviour of the substances. Often, again, the phenomena which precede fusion, accompany it, or succeed it, are of much determinative value. Thus topaz blisters on the surface, glassy bubbles forming and

breaking up which throw out viscous threads and emit a gas (fluorine?) which attacks the platinum, forming coloured rings upon the bright red metals: iolite turns milk-white. The presence of any considerable quantity of calcium oxide produces this latter effect. Labradorite may be distinguished from the other felspars by this phenomenon. Orthoclase at high temperatures develops large bubbles—which seldom break—throughout the clear viscous liquid into which it is transformed. Tourmaline boils easily, often with effervescence at first, ultimately settling into a quiet boil. Pyromorphite flows into an oily-looking liquid, part of which runs along the ribbon till it attains a cooler region near the forceps, where it pulsates backward and forward,—a surface tension phenomenon. On cooling it is seen that a double-coloured slag is produced as if a separation had been effected. Molybdenite sublimes, building up a frail, skeleton-like structure over the ribbon, which consists of glistening, tabular, colourless crystals. These again re-sublime to similar crystals if tumbled back upon the platinum.

Some substances show a change of colour when first heated, as realgar, which blackens, and beryl, which bleaches. Some remain viscous to the last and have no definite melting-point, but gradually soften. Beryl is a case of this, and the felspars, in a less degree, possess the property. Other minerals break down comparatively suddenly and flood the platinum, as garnet, tourmaline, &c. Finally, the colour of the melted mineral—whether a slag or a glass—affords distinctive characters as in the blowpipe, but in a more extended degree inasmuch as the range of temperature is greater under perfect control, and the method more cleanly in use, uncomplicated by secondary effects, and the substance is under much better conditions for observation.

As regards the determination of melting-points in Centigrade degrees by the use of this simple form of apparatus, the closeness with which we can approximate to a true estimate depends on our ability to map out the range of temperature at our command with reliable and sufficiently varied standards of reference. As the construction of such a table or scale of melting-points should be based upon the widest possible experience, I do not suggest any complete scale here; but in the second part of this paper will endeavour to rectify the omission.

Meanwhile, it will be found on reference to Carnelley's "Melting and Boiling-Point Tables," or the "Tabellen" of Landholt and Börnstein, that a wide choice exists of comparative substances up to a certain range of temperature, from the determinations of Violle, Carnelley, and others on metals and pure salts. The scale will have to exclude as far as possible substances which undergo a period of viscosity before decisively melting. To such substances no definite melting-point can, of course, be assigned, and the temperature at which they begin to soften is not well defined.

If direct observations of the phenomena progressing upon the hot platinum be resorted to, we obtain for viscous bodies temperatures of melting much above, often by some hundreds of degrees, the softening point, *i.e.*, a point at which particles soften sufficiently to adhere to the platinum. In fact the earlier stages of softening appears still attended with an amount of rigidity competent to delay any considerable displacement of the lower particles an indefinite time. A much higher temperature is required to cause these lower particles to liquefy and permit of the spreading of the mass. This is the state of things when fusion becomes visible. The lower particles are then in such a state of aggregation as to yield to a small distorting force within a small interval of time. This appears to be a truly fluid state, and I have called it the melting point or melting interval. Thus if the temperature is such that within three or four minutes we perceive the finer dust rounding into little drops the melting point is attained. The temperature of softening is defined as that at which the lower particles begin to adhere to the platinum. It is evident that this

will only occur when their original configuration is broken up. These particles are, of course, those most nearly at the temperature of the platinum. To determine this interval we proceed as follows. When the substance has been exposed for four or five minutes to a particular temperature, the current is stopped and the cool ribbon washed with a sable-hair brush moist with water. A high power—a half-inch is suitable—is then brought to bear upon the site of the powder. Glassy fragments adhering to the platinum indicate that a temperature not lower than the softening point has been attained. After three or four trials the softening range is determined within sufficiently narrow limits. In these trials a very small quantity of the substance may be used, as a high and good power is permissible, no observations being made while the ribbon is heated. The microscope-tube should be simply racked up while heating is going on, so that, when the current is stopped and the ribbon cleaned, the site of the powder may be formed with certainty by again bringing the objective into focus.

In the case of non-viscous bodies the temperatures of softening and melting sensibly coincide. There is instant breakdown and flooding upon the platinum.

(To be continued.)

A TABULAR EXPRESSION OF THE PERIODIC RELATIONS OF THE ELEMENTS.

By HENRY BASSETT.

At the present time the Periodic Law of the Elements is becoming universally accepted as the basis of the study of their relative properties and individual peculiarities; and Prof. Mendeleeff's tabular arrangement is very generally adopted for its illustration in modern chemical books. Having been for some time past much interested in the subject, I have been impressed with many anomalies in the table in question, some of which are generally known and admitted; but as I venture to think I have arrived at a more comprehensive and satisfactory expression, I will point out some few of the anomalies to which I refer.

At the first glance we cannot help being struck by the great blank space in the fifth column. We have no indication of the existence of any metals between Ag and Au downwards, which is at least very remarkable; the same may be said as to the platinum metals, which have been very thoroughly investigated, and are always associated in nature, but only the six are known.

According to their atomic weights, many of the so-called rare earth metals should find their places here, but their properties are absolutely incompatible with such a position, as was pointed out by Crookes in his address to the British Association in 1886, from which I will quote the following:—

"Judging from my own researches, it is probable that many of these earthy elements will be found included in one or more interperiodic groups, whilst . . . the elements between Ag and Au, Cd and Hg, In and Tl, &c., &c., are still waiting to be discovered."

Another difficulty occurs with Yb, one of the least basic earths, which follows La, the most powerfully basic of all; we also see Di, forming a strongly basic oxide, separating Nb and Ta. Again, we find U, which, like the earth-metals, can only be obtained by reduction of its chloride by sodium, allied to W, which is reduced by hydrogen at a red heat.

I will now call attention to the following table, which, with its derivatives, seems to meet the difficulties to which I have briefly alluded, and which simply amounts to an alteration in the position of Mendeleeff's ninth group, and the addition of one interperiodic group.*

* Though at present we actually know but three of these interperiodic groups, it seems not unreasonable to regard them as the *raison d'être* of the large periods, acting as connecting links between the component small periods.

The atomic weights are Prof. Clarke's, to the first decimal, except in the case of three or four rare elements which are not included in his table of Dec. 6, 1890.

Cs 133	226?
Ba 137	?
La 138 ²	?
Ce 140 ²	Th 232 ² 6
Ndy 140 ⁸	?
Pdy 143 ⁶	U 239 ⁶
148?	241?
Sm 150	?
?	?
?	?
154?	248?
?	?
Tb 159 ⁵	?
Ho 162	?
?	?
Er 166 ³	?
169?	263?
Tm 170 ⁴	?
Yb 173	

K	39.1	Rb	85.5	174.3
Ca	40	Sr	87.6	?
Sc	44	Y	89.1	?
Ti	48	Zr	90.6	?
V	51.4	Nb	94	Ta 182.6
Cr	52.1	Mo	96	W 184
Mn	55		100?	189?
Fe	56	Ru	101.6	Os 191.7
Ni	58.7	Rh	103.5	Ir 193.1
Co	59	Pd	106.6	Pt 195

Li	7	Na	23	Cu	63.4	Ag	107.9	Au	197.3
Be	9	Mg	24.3	Zn	65.3	Cd	112	Hg	200
B	11	Al	27	Ga	69	In	113.7	Tl	204.2
C	12	Si	28.4	Ge	72.3	Sn	119	Pb	207
N	14	P	31	As	75	Sb	120	Bi	208.9
O	16	S	32.1	Se	79	Te	125		?
F	10	Cl	35.5	Br	80	I	126.9		216.9

I must now give a quotation from Professor V. von Richter's "Inorganic Chemistry" (p. 247 of the third

The second fold of the paper round the cylinder covers up all but the two left-hand small periods, and gives rise to the following :—

Li	Na	K	Rb	?
Be	Mg	Ca	Sr	?
B	Al	Sc	Y	?
C	Si	Ti	Zr	?
N	P	V	Nb	Ta
O	S	Cr	Mo	W
F	Cl	Mn	?	?

(To be continued).

(Continued from p. 315).

* In this and the two following tables, the atomic weights are omitted for brevity.

methyl chloride into the mixture of aluminium chloride with benzol, hydrochloric acid is given off, and there is chiefly formed durol or tetramethylbenzol. Toluene, if similarly treated, yields dimethylbenzols, trimethylbenzols, tetramethylbenzols, pentamethylbenzol, and hexamethylbenzol. . . . What part is played by aluminium chloride in these complicated reactions we do not know."

We give an example that many more complicated syntheses are effected in chemical industry in presence of condensation processes, and not as mere by-reactions, but with a remunerative yield. If we treat dimethylaniline with phosgene, in presence of aluminium chloride, we obtain tetramethyldiamidobenzophenon. This body can be further condensed with other bases by the addition of condensing agents, *e.g.*, with phenyl- α -naphthylamine, and there then results α -naphthyltetramethyltriamidotriphenylcarbinol, a base the double salt of which is the Victoria blue, a colouring matter highly valued for cotton-dyeing. In many condensations the reactions are so complicated that we are left completely in the dark.

Chemistry has hitherto been content resignedly to put forward a few very doubtful and mutually contradictory equations of reaction (Friedel and Crafts; Gustavsen), but without a single attempt to obtain a clear insight into the quite peculiar conditions, and, consequently, into the peculiar forces in such condensations, which cannot be in any manner explained by chemical affinity.

Sulphuric acid, in which the especially strong by-reactions which have nothing whatever in common with condensation indicate more complicated relations, cannot be here drawn prominently into consideration, the rather as it is now rarely used in the condensation of colouring matters. But Menschutkin has shown even for "quite indifferent" solvents that strong by-reactions must occur in consequence of their solvent power, even if we leave out of account the chemical reactions which arise. These solvents are falsely named "indifferent," as the reactions are undoubtedly connected with their chemical nature.

Condensation agents, such as aluminium chloride and bromide, zinc chloride, sodium disulphide, phosphoric anhydride, possess two characteristic attributes common to them all:—

1. They all rank among the most highly hygroscopic substances.

2. In their anhydrous state they are exceedingly porous.

As hygroscopicity is common to all porous bodies a relation must exist between these two properties.

In comparison with the above-mentioned condensations may be adduced one—and indeed the simplest—of such unexplained transformations discovered by chemical industry, *i.e.*, the process for obtaining chlorine by passing dry gaseous hydrochloric acid and dry air over heated bricks. This process was indicated by Oxland in 1847. Here we cannot doubt but that the effective substance is the third porous body, the action of which, as subsequently shown by Deacon, can be much heightened by impregnation with metallic salts, especially copper sulphate. As Deacon's process comes into action only at temperatures exceeding 200°, at which temperature copper sulphate is rendered anhydrous—a circumstance which is here pointed out probably for the first time—the active body in this simple but astonishing chemical transformation is a highly hygroscopic and porous body.

Of what nature are the forces which are capable of calling forth all these mighty transformations even in the most stable compounds?

According to Bunsen, the tension in fine films of water, on fine glass tubes, amounts to hundreds of atmospheres, whence is explained the exceedingly strong absorption and condensation of carbon dioxides in such films. According to Joulin, ammonia is absorbed by wood charcoal with a tension of 246 atmospheres.

(To be continued.)

NITROHYDRIC ACID.*

By TH. CURTIUS.

(Continued from p. 314.)

AFTER the solution has become cold the substance appears in shining colourless needles of a centimetre in length deceptively similar to those of lead chloride, but which if gently heated explode with fearful violence. On prolonged boiling in water, the lead salt is very gradually decomposed with the separation of a lead compound which is not explosive. By holding over it a glass rod, on which is placed a drop of a solution of silver nitrate, it may be plainly seen that nitrohydrogen is being volatilised as the drop is rendered turbid by the deposition of silver nitrogen. Nitrogen lead dissolves readily in hot acetic acid, and is gradually decomposed with liberation of nitrohydrogen. It is insoluble in concentrated aqueous ammonia.

Nitrogen Sodium, N_3Na .

This compound is obtained by neutralising the free acid with soda-lye, by adding sodium hydroxide to the ammonium salt, and concentration on the water-bath. It is most conveniently obtained by the action of sodium alcoholate upon benzyl nitrogen in an alcoholic solution. $C_6H_5CON_3 + C_2H_5ONa = N_3Na + C_6H_5CO_2C_2H_5$.

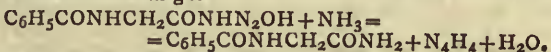
The salt may be re-crystallised from water, or precipitated by adding alcohol to the aqueous solution. In order to determine the proportion of nitrogen in this compound it is necessary to burn it mixed with lead chromate.

		Found per cent.	
		I.	II.
N_3 42	 64.62	64.70	—
Na 23	 35.58	35.29	35.62
65	100.00	99.99	—

Nitrogen sodium is readily soluble in water, but insoluble in ether and alcohol. It has a slight alkaline reaction and a very saline taste. It does not explode on percussion, but only if heated to a very high temperature. It burns with brilliant yellow light and a faint detonation.

Nitroammonium, N_4H_4 .

This salt, as it is above described, is directly obtained by saturating an alcoholic solution of diazohippuramide with ammoniacal gas—



Ether precipitates pure nitroammonium. This compound can be re-crystallised from boiling alcohol. The proportions of nitrogen and hydrogen were conjointly determined by combustion with copper oxide in a current of carbon dioxide. The water which is formed is absorbed in the chloride of calcium tube. Extraordinary caution must be used on account of the great volatility of the substance. But even if perfectly dry carbon dioxide is passed very slowly through the apparatus, the volume of hydrogen obtained is often deficient.

If we endeavour to burn nitroammonium in a current of air in presence of copper oxide, the apparatus is invariably shattered with a fearful detonation. 0.1 gm. of the substance destroys a platinum boat, only a few flattened splinters being left. The compound sublimes at first very finely from the boat into the colder combustion tube. As the temperature rises the crystals are converted into yellow drops. As soon as this point is reached the explosion follows in a few moments. It is conceivable that the compound N_6 is first formed by oxidation and then explodes with extreme violence.

The composition of this substance is:—

		Calculated for $N_4H_4.NH_3$.	Found.
NH_3 17	 28.83	28.00	
		(To be continued.)	

* *Berichte der Deutsch. Chem. Gesell.*

THE PURIFICATION OF WATER.*

By Professor ALBERT R. LEEDS.

COMPARING the composition of the waters obtained on the 2nd of May, at noon, from the Genesee River at Elmwood Avenue Bridge, and that from the conduit at Mount Hope reservoir, Professor Leeds stated that the water from the Genesee River had a slight yellow colour, due to peaty matters in solution, and was slightly turbid. It had a flat taste and a slight odour. That from the Mount Hope reservoir was colourless, but manifested a whitish turbidity; it was pleasant to the taste and had no odour. The Genesee water contained 0.044 of a grain of free ammonia per gallon; the Hemlock, 0.032. The Genesee water contained of albuminoid ammonia, with organic nitrogen, 0.071 of a grain; the Hemlock, 0.078, slightly more. The Genesee water required to oxidise the organic matter, 0.147 of a grain of oxygen, the Hemlock Lake, 0.136 of a grain, or something less. The difference was due to these peaty organic matters in solution, which require a slightly greater amount of oxygen to oxidise them. The hardness of the Genesee water was 6.85 grains; the Hemlock Lake, 3.2. The total solids in solution in the Genesee water were 16.47 grains; in the Hemlock Lake, 5.08 grains. A count of the bacteria contained in the waters showed that there was in the Genesee River water 112 colonies of bacteria to the cubic centimetre; in the Hemlock Lake, 63 colonies. The samples were sent to me in jugs labelled 1 and 2, and at the time of making the analysis I did not know to which samples the numbers referred. The analysis showed that No 1, the harder water, of course, came from the river. And I shall now label these bottles containing a portion of that water. And, in the first place, there is the Genesee water. Mr. President, you will notice this limpid matter in it. Perhaps you can see it.

After making the analysis, for reasons which I will explain presently, I added to each water a grain of sulphate of alumina, and then filtered the samples through sand. This marked No. 1 is the filtered Genesee water; 2, the filtered Hemlock. I do not think that it is possible to notice any difference. Both of these samples are as entirely limpid, entirely colourless, as the purest distilled water that I could make in my laboratory. They are absolutely devoid of any colour and any odour. The whitish opalescence, or the whitish turbidity, has been removed from the Hemlock water; the yellow from the Genesee water.

This brings me to the treatment of waters by filtration. And at the outset I would like to say that I know of no method by which it is possible to render waters organically pure except by filtering; and, in the second place, I know of no practical method of bringing about that result except by the American system of mechanical filtration and purification. As these statements appear strong and unqualified, I think it is important that I should briefly review the history of our knowledge and practice during the course of the past ten years, in relation to this subject.

Some six years ago there was, I think, but one city in the United States which attempted to filter its water, and that was Poughkeepsie on the Hudson. At the present day there are more than one hundred, and the practice is increasing very rapidly. In England, and on the continent of Europe, the practice of filtration is well nigh universal. Some five years ago Jersey City and Newark, in New Jersey, requested me to visit the various water supplies, in England more especially, to study this matter of filtration of their waters, and I found that all the great cities, with the exception of Glasgow, filtered their water supplies. The most conspicuous example is London,

with its population of five and a half million of people. Its water supply is almost entirely taken from the River Thames, and that river receives the drainage of a very great population. The towns are compelled, by Act of Parliament, to purify their sewage to a certain point, but a great deal of filth finds its way into the Thames. By Act of Parliament the several water companies that supply London are compelled to filter their water; and to effect that object they have filter basins which cover more than a hundred acres in area. Their method of filtration is to run the water into large reservoirs containing sand. The sand that does the filtering is about two feet in depth, and supported on a substratum of coarse stone. As the filth is removed it accumulates in a thin layer upon the top of the sand; and when the water—which filters only under the pressure of the four feet, or thereabouts, of water standing in the reservoir—filters too slowly, they are compelled to send a force of men into the filter basin, shovel off the top layer of sand and dirt, remove it, wash it, and restore it to the filter bed. The same plan is followed at Berlin and other great cities on the Continent.

How the Filter Beds do their Work.

It is easy to see how they remove the dirt, the gravel, and the suspended matter; but how do these shallow basins of sand remove the living organisms—those organisms with which you are all so familiar under the name of bacteria; those organisms which, when they produce typhoid and other fevers, are known as disease germs? That operation was a complete mystery until the last four or five years. But few people had ever seen or examined bacteria before that period. It is entirely a new topic in this country; and the method by which they were removed from the waters was a profound mystery. It now has been shown that the bacteria remove the bacteria. The bacteria in the waters are comparatively few of a dangerous character; the great bulk of them are our greatest friends. It is through their aid, together with the oxygen of the air, that the filth in the water is destroyed. They feed upon it, and they feed upon each other. Since that knowledge has been obtained, the object now is to cultivate the bacteria. In order to make the filter bed do its work effectively, it is necessary that the growth of the bacteria shall be facilitated until a filter bed becomes populated with an incredible number of millions of them. As the result of their activity they multiply themselves in vast numbers; and they form, at the top of the filter beds and between particles of sand, a sort of jelly or slime—a bacteria jelly; and it is by the aid of this bacteria jelly that the bacteria in the unfiltered water are removed. The bacteria come down into the pores of the filter, when they are caught by this jelly and they are consumed. And if the rate of movement of the water is slow enough it is possible to begin with water like that of the River Spree, which is a portion of the water supply of Berlin, containing 100,000 of bacteria to the cubic centimetre, and after passing through one of the filter beds the water which comes out will contain but forty or fifty bacteria. This takes place when the rate of filtration is such that 1,000,000 gallons of water pass through those filter beds per acre in twenty-four hours. If the rate is diminished until only 300,000 gallons pass through in that interval, the bacteria can be diminished until there are only five or ten per cubic centimetre. But this rate is too slow to permit of the economical use of the filter beds, and the consequence is that the authorities of Berlin require that the water shall pass through the filter beds at the rate of a million gallons per acre in twenty-four hours. The interesting fact is thus brought out that some of the foulest water, most polluted with sewage, is so filtered at the present day in the capital of Germany; the filtered water is submitted to the most searching criticism of Professor Koch, whose institute of hygiene is there, and to whose labour our knowledge on this subject is mostly due, and

* An Address delivered by Professor Leeds before the Chamber of Commerce of Rochester, N.Y., May 12, 1891.

that this foulest of water is there taken, filtered, and then becomes the water supply of Berlin. If we can do as well or better than that, we have every reason to be satisfied that we are on the side of safety.

The foreign filter beds, excellent as they are, have never been introduced practically in the United States. Moreover, there is no prospect that they will be. The amount of water filtered per acre is so small that the first cost is a large one. In the second place, the climate of Europe and of England is altogether different from the climate of America. Those filter beds freeze up, even at London, and the engineers are sometimes greatly troubled. In the next place, in England, even in that temperate climate, a great quantity of *Algæ* develop in the filter beds. In the United States, with our severe winters and the great trouble you have experienced in Hemlock Lake, from the growth of *Algæ*, engineers are unwilling to undertake such method of filtration. This being the case, the attention of engineers has been directed to find some way of effecting a result which will satisfy our own needs. And the system that I shall bring to your notice in reference to your immediate wants is this American system.

The filter is simply a case made of boiler iron, of 5 ft., 10 ft., or 20 ft. in diameter, made strong enough to stand any pressure to which it is subjected. It contains a bed of sand 3½ or 4 ft. in depth. The water is passed through the filter under pressure, and passes out of the bottom by a series of valves so constructed that they permit the water to pass, but entirely detain the sand. After a time, when the filth accumulates on the surface and through the bed of the sand, the operation is reversed, a current of filtered water under pressure is sent up from below, the sand is washed, and the impurities pass out from a waste pipe, and then filtration is resumed. In practice, after filtering for ten hours, a filter operating on such water as the Genesee River can be purified by washing in ten minutes' time.

That it is possible by such a method to renovate the sand and dirt you will probably have no difficulty in admitting; but what will such a filter do with reference to the bacteria? If it is necessary to pass water at so slow a rate where the pressure is as light as that given by a head of four feet, as is the case in the foreign filter bed, how is it possible to pass the vastly greater quantity through one of these American filters? One of these filters of which I have been speaking, ten feet in diameter, under a pressure of 15 lbs. to the square inch, will filter successfully a quarter of a million of gallons per diem. In order to effect that result it is necessary to have something which will take the place of the bacteria jelly that I have described. And the most successful substitute is a jelly made of hydrate of alumina. It is obtained in this way. All natural water contains in solution carbonate of lime, to which its hardness is due. When sulphate of alumina is introduced into the water it is decomposed by the carbonate of lime, and sulphate of alum is formed and hydrate of alumina is set free. It is a perfectly white translucent jelly. It forms on the surface of the filter bed in contact with the grains of sand, and when the smallest particle of silt or the bacteria come in contact with it they are caught by it and held. It is possible to entirely remove the bacteria from water by use of this jelly. These filters, worked in that manner, have been repeatedly tested, and that point has been most carefully established.

The water that I have sent around the audience this evening is filtered water. It contains no bacteria. They were removed at the same time that the turbidity and the colour were taken out. The question then is, whether the bacteria are to be removed by a bacteria jelly or by means of an alumina jelly. There are some who think that no chemical substitute whatsoever can rightly be employed in the purification of water. It appears to me to adopt such a sentiment is to renounce the advantages which the very elaborate study of this question has given

to us. They say that hydrate of alumina, which is one-fourth of alum, is very pernicious to health. If alum ever went into your water supply I would concede the point that it is not a proper thing to use; but it does not go into the filtered water. The alum is so perfectly decomposed that I never have been able to find it in the filtered water. The hydrate of alumina is left behind, and the alumina which goes into your water in a minute amount is also present in natural water itself. If you examine the analysis of the river water you will find that the water contains naturally some alumina. It is the alumina in the soil which makes spring water so bright. It is the alumina in the soil which makes the water of driven wells filtered water. All that is proposed in this method is to take advantage of Nature's methods.

In the sample that is before you a quarter of a grain of alum has been used. That is so small an amount that it is difficult to weigh it upon a druggist's balance. Of that quarter of a grain of alum, only one-third is alumina; and one-twelfth of a grain of alumina, or the 1-700,000th part of the weight of a gallon of water, is sufficient to remove all the dirt and all the bacteria by this process of filtration. The quantity is practically infinitesimal.

Unfortunately, the Genesee water, at the time it was sent to me, was in a very favourable condition. I wish it had been at its worst, because the difference is too slight to show what the process is capable of doing. This method is now in use supplying filtered water in much larger quantities than what you desire to have here. The City of Chattanooga, some four years ago, began taking some three million gallons of water from the Tennessee River. It has now gone on increasing its filtering plant, until it takes six million gallons, and it is all treated by the method I have spoken of. I have here a sample of water taken from the Wabash River at Terre Haute. It is not possible that the Genesee River should ever have water of the character that you see here. It is loaded with mud. The water was so bad that I at first thought, when this sample was submitted to me, that it was a hopeless case. I am interested in this question, as a consulting chemist, from the fact that a great many waters are submitted to me by the people that are engaged in doing this work, and I am desirous of seeing this American system introduced generally. I think it will be universal before many years have passed. And here is one of the samples that was submitted. A plant was put in some year and a half ago to filter this Terre Haute water. The impurities were so great that I said that they could not be successfully handled without using as much as four grains of alum to the gallon. They have been filtering not three, but four and a half million gallons of water with a three-million-gallon filter plant. And this has been done with two grains of alum to the gallon, and less. The superintendents have been careful not to use more than that, because of the expense. They use less. And this is the largest amount of alum I have ever known to be used practically in the filtration of water.

I will not detain you longer than by saying I have here a working drawing, showing ten of these vertical filters, ten feet in diameter, which are doing this work at Terre Haute. The water is filtered under a pressure of two hundred pounds, and the filtered water is used for fire purposes as well as for general supply.

Here is the working drawing of a plant at a place in Kansas: a smaller plant. It is the same size as that at Bordentown, in New Jersey. Long Branch has for the past three years filtered and treated all its water in that way. It was much more deeply coloured with peat than the Genesee River water was that came to me, or, it is possible for the Genesee ever to be coloured. It came from a Cypress swamp. And the filtered water at Long Branch is colourless. And when the health inspector of Providence examined that plant he found that the filtered water contained two bacteria per cubic centi-

metre, while the unfiltered water contained three hundred.

In conclusion, then, I will say that this method is in use in one hundred of our American towns; that those who are using it are extending their plants to supply the increased demand; that by its use in the filtered samples which I have shown you, the organic nitrogen in the Genesee water was cut down to one-half the amount usually present, and also the water in the Hemlock Lake was cut down by the same amount. The Hemlock water, if filtered by this method, would be 100 per cent purer than delivered to you as it is, and you consider it, as it is, very excellent water.

At the recent convention of the engineers in Philadelphia the expression of opinion was general that this method of treatment of waters was, in the near future, to be generally adopted. When the city of Liverpool put in its new water supply from Vyrnwy Lake, the purest water they could obtain in Wales, they put on the descending main a filter plant; and I said to the chief engineer at Liverpool, "Why do you filter this beautiful mountain water?" and he said to me, "The public opinion in England is so strong in this matter that we cannot supply water unless it is filtered." If you have examined one of those filter systems you will find that all of the filtered water is passed through a well, at the bottom of which there is a pavement of white porcelain, and the engineer and the people are not satisfied without, on looking through a depth of five feet of water, the filtered water should always go over that porcelain and be absolutely colourless. I think the time has gone by in this country when people will be satisfied with taking any water supply without they are made certain of its purity. As I said before, I know of no method of guaranteeing the purity of water except by filtration.

Mr. President, I trust I have been not too lengthy, I wished to answer the question which was asked: "If a temporary supply of 3,000,000 gallons of water is taken from the Genesee River, can it be made colourless?—can it be made pure from a sanitary standpoint?" I have answered that it can be, and that the method is one in large use, and is a method requiring so moderate an outlay that it has become feasible for the water supply of cities demanding a great amount of water.—*The Stevens Indicator*, viii., No. 42.

ON THE DECOMPOSITION OF MINERALS CONTAINING TITANIUM.

By JESSE JONES.

IN attempting to conduct the analysis of a very refractory mineral containing titanium, magnesium, chromium, &c., according to the method given by Chatard (*Journal of Analytical and Applied Chemistry*, v., 163), it was found very difficult to secure complete decomposition of the mineral by the use of hydrofluoric and sulphuric acids as detailed. Repeated fusions with potassium pyrosulphate while decomposing the mineral introduced large quantities of salts, and was very tedious.

These difficulties led me to seek some method that would give more satisfactory results. The following was finally adopted: 2 gms. of the mineral were placed in a pressure bottle, to which was added 20 c.c. of water and 20 c.c. of strong sulphuric acid. The ground-glass stopper not fitting air-tight, a small sheet of pure rubber was interposed. The bottle and contents were placed in an ordinary air bath, and kept at 200° C. for two hours. The residue weighed 0.018 gm., and was mainly silica. On treatment with hydrofluoric acid, but 0.002 gm. of residue remained. A temperature of 200° C. was found to melt the rubber somewhat, but a longer exposure at a lower temperature gave equally good results. As the resulting solution showed a tendency to gelatinise, water

was added to it, taking care not to allow it to touch the heated sides of the bottle. The refractory nature of the rock may be judged from the fact that it contained over 7 per cent MgO, 14 per cent Al₂O₃, and considerable amounts of titanium and chromium, which have not yet been determined. By using ammonium salts in the subsequent operations, they can be expelled by nitric acid, and potash and soda, if present in the mineral, can be determined.

If a pressure bottle is not at hand, one can easily be improvised. The writer found an old bromine bottle sufficiently strong.—*Journal of Analytical and Applied Chemistry*, v., No. 11.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

December 18th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MR. R. W. MOND, F.R.S.E., was elected a Member of the Society.

The PRESIDENT announced that it had been found necessary to alter the dates of the meetings to be held after Christmas from those already published to the following:—Jan. 22, Feb. 12 and 26, March 11 and 25, April 8, May 13 and 27, June 10 and 24.

A "Note on Interference with Alternating Currents" was communicated by Mr. M. H. KILGOUR. Whilst studying Dr. Fleming's paper on "Some Effects of Alternate Current Flow in Circuits having Capacity and Self-Induction," the author constructed some additional curves. He was thereby led to investigate whether the serious rises of pressure produced by adding capacity would occur over considerable ranges of capacity, or whether they would only take place when the capacity was nearly equal to a particular value. Taking the case of a condenser of capacity C farads, in series with a circuit of resistance R ohms and inductance L henrys, he showed that the maximum value of λ (the ratio of the pressure across the condenser terminals to that across the condenser and inductive resistance) is obtained when

$$C = \frac{L}{R^2 + p^2 L^2} \quad (1), \text{ where } p = 2\pi \text{ times the frequency.}$$

The maximum of λ produced by this capacity being given by the expression—

$$\Lambda = \frac{\sqrt{R^2 + p^2 L^2}}{R} \quad (2).$$

Taking $R = 10$ and $p = 2\pi \cdot 1000$, curves plotted from equations (1) and (2) between C and L, and between Λ and L, had been drawn. The CL curve rises to a very sharp peak at $L = 0.0015$, and falls rapidly. That between Λ and L starts horizontal and bends upwards, and approximates to an inclined straight line for values of L greater than 0.002; when $L = 0.1$, $\Lambda = 63$.

Considering the question of the range of capacity with which a given rise of pressure can occur, it was pointed out that when the value of L, R, and p are such as to make a large rise possible, a rise exceeding a moderate value can only be obtained for values of C differing little from that given by equation (1). On the other hand, when the circuit is such that the maximum rise possible is not large, then a rise exceeding a given moderate value can be obtained over a much wider range of capacity. Hence the author concludes that the larger the possible rise, the smaller is the probability of a serious rise occurring.

The effect of shunting the condenser by a circuit of resistance r and inductance l is next dealt with in the paper, and the values of C which make λ a maximum determined, as well as the maximum value λ can have.

Subsequently the author examines whether the practical

case of an alternator feeding a transformer through a concentric cable may be simplified without introducing serious error, by assuming the capacity concentrated at either end of the cable, and concludes that in ordinary cases little error will be thus made. In an experiment made with a 100 kilowatt alternator, $\frac{3}{4}$ mile of $\frac{1}{2}$ inch concentric cable, and an 18 kilowatt transformer, a rise $\frac{1}{2}$ per cent was found to occur at the terminals of the alternator when the cable was connected. Putting on the transformer unloaded or loaded produced little change in the rise of pressure, this in all cases being between 0.2 and 0.3 per cent.

Dr. SUMPNER asked whether the conclusions as to the range of capacity with which a given rise of pressure was possible was true for small rises such as occur in practice. Cases where the maximum possible rise was of the order 63 were not likely to occur at ordinary frequencies. The highest rise he had ever known was 11. He thought the time λ constant of the inductive coil chosen, viz., $\frac{1}{100}$ of a second, was very large. In circuits containing iron it was practically impossible to get such large time constants, for the power spent in the iron increased the effective resistance. Referring to the narrow range of capacity, within which large rises were possible, he pointed out that such cases were found in Hertz's resonators, where the rises were immense, but to obtain them the adjustments had to be very accurately made.

Dr. S. P. THOMPSON said he regretted that Professor Fleming was not present, for he had recently investigated Hertz's experiments and had obtained curves very similar to those got for the Deptford mains.

The curve between Λ and L was very interesting. It was, in fact, a curve between the secant of the angle of lag and L , as could be seen from formula (2). In practice one would be working on the lower portion, and hence the rises would be small.

Mr. KILGOUR explained that in the paper his first object was to show that the product of the range of capacity between which a rise greater than a given value would occur, and the maximum possible rise, was approximately constant for different circuits. Secondly, he wished to prove that the capacity of concentric cables could be assumed to be localised at either end without introducing much error in the rises of pressure calculated therefrom.

Dr. THOMPSON, speaking of nomenclature, regretted that the word inductance should be used sometimes for L , and at other times for L_p , and thought its meaning should be restricted to the latter.

Prof. PERRY said a name was needed for co-efficient of self induction. Resistance was practically independent of frequency, and "inductance" should have no reference to frequency.

Dr. SUMPNER thought it important to have a name for L_p , for that quantity comes into calculations most frequently. He would have preferred that "inductance" should mean L_p , but Mr. O. Heaviside, who introduced the term, had used it for L .

The PRESIDENT remarked that some time ago Dr. Sumpner and himself felt the need of a name for L_p , and thought of using "inductance," but on referring to Mr. Heaviside's articles found it used for L .

Dr. C. V. BURTON asked whether the word "self-induction" could not be used as an abbreviation for "co-efficient of self-induction."

Dr. THOMPSON pointed out that this word already had a meaning, viz., L multiplied by current.

Dr. BURTON then suggested that inductivity might be applicable.

Dr. THOMPSON said the word "impedance" was also used ambiguously, for the sense in which Dr. Lodge uses it, in his "Modern Views of Electricity," is not the same as the vector sum of R and L_p .

Prof. PERRY recalled the fact that "impedance" had been defined by the Committee of the British Association as the ratio $\frac{\text{Effective voltage}}{\text{Effective current}}$.

Dr. THOMPSON said this definition was only applicable to periodic currents and not to intermittent or transient ones.

The PRESIDENT said he understood the first object of Mr. Kilgour's paper was to enquire whether the dread of rise of voltage occurring when concentric mains were used, need exist. When Dr. Fleming's paper was read, the general idea was that concentric cables were dangerous. In the discussion on it, he, amongst others, had pointed out that the chance of a large rise of pressure was not a serious one. Mr. Kilgour had now shown that the range of capacity over which a particular rise could occur is inversely proportional to the maximum rise possible in the particular circuit. When the circuit was such that a large rise was possible, the probability of any serious rise taking place was very small; hence, the fears of large rises were more or less unfounded.

The second part of the paper was to show that ordinary problems on concentric cables could, in practice, be treated with sufficient accuracy by assuming the capacity localised at either end of the cable, instead of being distributed its length.

NOTICES OF BOOKS.

The Metallurgy of Argentiferous Lead. A Practical Treatise on the Smelting of Silver-Lead Ores and the Refining of Lead Bullion. By M. EISLER, Mining Engineer and Metallurgical Chemist. With 183 Illustrations. Crown 8vo., pp. 396. London: Crosby Lockwood and Son.

Mr. M. EISLER's former works on the metallurgy of gold and of silver have given such general satisfaction that the present volume may be sure of a favourable reception. But it may well claim the right of standing on its own merits, which are undeniable. In his introductory chapter the author gives a general survey of the occurrence and distribution of this metal. It is very commonly accompanied by silver, and seems to have a predilection for calcareous rocks in whatever geological formation they may be found. In short, various and extensive as are the applications of lead,—in some cases deplorably so,—there is no reason to expect that the supply may fall short.

The author then discusses in succession the reduction of lead ores in reverberatories, the smelting of lead ores in blast furnaces, the construction of such furnaces, water jacket furnaces, the process of smelting, and the roasting of lead ores. Hence we encounter the same three modifications as in the case of copper ores, heap-roasting, stall-roasting, and kiln-roasting. The proportion of sulphur is so much smaller in lead ore than in iron and copper pyrites, that galena alone cannot be used to feed the chambers. Sometimes, however, the matte produced in smelting is mixed with lead ores containing foreign sulphides, when the mixture may be burnt in a kiln.

The next chapter treats of the products of the smelting operation, the crude lead being called bullion,—a name which has heretofore been restricted to the precious metals. Upon the condensation of lead fumes the author insists strongly. Unlike Mr. Peters, he holds that ores which contain antimony and arsenic "will so vitiate the atmosphere around the locality of smelting-works as to produce a most pernicious effect not only on animals but also on vegetable life." We certainly incline to his view rather than to that of Mr. Peters. At all events, when public health is concerned we should keep on the safe side, and if a doubt exists we should rather be too stringent than too lenient. The condensation of metallic and other fumes by electric action (Walker's process), is described, but Mr. Eisler does not pronounce on its efficiency.

We come next to the separation of silver by cupellation, the extraction of silver from lead, and the refining of silver-lead, and lastly to the assay of lead ores and their products. Here we find that the dry method is advocated on the same grounds which English smelters advance for retaining the Cornish assay for copper, *i.e.*, that it is a repetition on the small scale of the treatment which the ore will have to encounter in actual practice. This plea we must reject as invalid. The losses will always be found proportionally larger the smaller the scale of operations. Again, it is important for the smelter to learn how far he falls short of extracting the total metal which exists in the ore.

There is an appendix which contains, *inter alia*, the conclusions of M. Guyard (Hugo Tamm) on the smelting operations at Leadville. Here we find the statement that there are detected in the ores "traces of tin, bismuth, cobalt, indium, selenium, tellurium, and a new metal which has been imperfectly studied as yet, and which appears to lie intermediate between the metals of the iron-group and those of the lead-group."

M. Guyard finds also "that a very curious and hitherto unsuspected reaction takes place in the blast furnaces of Leadville, by means of which cobalt is completely separated from nickel (nickel being concentrated in speiss and cobalt in the skimmings of the lead pots of blast furnaces), showing that the metallurgy of both metals and their separation could be effected in lead furnaces by operating under conditions similar to those observed at Leadville."

Whoever wants to acquire a clear insight into the metallurgy of lead will do well to study this volume.

Electricity up to Date, for Light, Power, and Traction.

By J. B. VERITY, M.I.E.E. London and New York: Warne and Co.

THIS work is very fairly entitled "Electricity up to Date," and contains certain features which ought to recommend it to the general public. A very useful one is the account given of the various companies which have undertaken the supply of electric current in London for the production of light and power. How far these companies may succeed, from a commercial point of view, is a riddle which has not yet found its *Œdipus*. The account given of the Board of Trade regulations concerning electric lighting will also be useful. The author, in his remarks on overhead conductors, seems to speak more in the interest of the supply companies than of the public, whose interest must, of course, be accepted as paramount.

The remarks on "electric engineering as a calling" will, we hope, act in certain directions as a much needed "wet blanket." In these days there is no such thing as "an unworked lode." We read here—what we know to be the truth—that "there is at present nothing like sufficient work for the enormous number who have drifted into electrical engineering during the past four or five years through every conceivable channel."

Mr. Verity gives also little encouragement to the many who cling to the hope that electricity may some day deliver us from steam and its attending nuisances. He writes that "the dynamo affords the most economical means of producing electricity, and will probably continue so to do." But save in those exceptional cases where water-power is available, the dynamo means coal-smoke, soot, ashes, coal-mines, and coal miners, with strikes, rings, and all the other machinery of modern industrialism.

Modern American Methods of Copper Smelting. By E. D. PETERS, Jun., M.E., M.D. Second edition, revised and enlarged. New York: Scientific Publishing Company.

METALLURGY seems at present to be attracting more attention than any other department of industrial chemistry. The work before us is a favourable result of

this tendency. To European, Australian, and probably African miners and smelters, a thorough practical insight into what is being done in the United States will be of unquestionable value. The only drawback is that the working cost of the various processes, the outlay for labour, fuel, and all other materials consumed, are based upon American prices and general conditions, and will hence be no certain guide in other localities.

The question of the assay of copper forms the subject of an ably written chapter. Four methods are described, the volumetric process with potassium cyanide, the precipitation method with zinc or iron, the colorimetric process, which the author recognises as adapted mainly for slags and tailings, and lastly the electrolytic process, which is, justifiably enough, the author's favourite. The conditions under which the cyanide process becomes untrustworthy are laid down very clearly. The author omits the Cornish assay, though he assigns a wrong reason for so doing.

Copper ore still seems to be very extensively roasted in the open air, or otherwise without absorption and condensation of the sulphurous acid given off.

Into the injuries occasioned by such fumes we need not enter, as they were thoroughly discussed whilst the Alkali Acts were under consideration. Mr. Peters fully admits that the only safe way of dealing with pyritic copper ores is to pass the gaseous products into chambers. Still there occur materials containing too little sulphur to be usefully burnt in the kilns, though enough to occasion a decided nuisance. It is here stated that the damage to crops and forests is caused solely by sulphurous and sulphuric acids, arsenical and antimonial fumes having no appreciable influence. It may reasonably be doubted whether arsenical fumes are totally inert as regards human health, and we may also ask if crops have ever been fully and persistently exposed to the action of arsenic and antimony in the total absence of sulphur fumes. The loss of copper by roasting the ores in heaps is said to be appreciable, about 1½ per cent on the assay value of the ores being thus sacrificed. As regards the cost of ore-roasting the information given is to any non-American exceedingly vague. The author speaks of what is done with a "cord" of wood. But to those who do not know whether a "cord" is a weight or a measure this is no information at all.

Whilst describing the roasting of ore in kilns Dr. Peters protests against the use of iron monosulphide. "It seems scarcely credible that extensive works for the manufacture of sulphuric acid and copper should have been erected, their ore supply being entirely derived from a deposit of the valueless monosulphide."

Ores in the condition known in Britain as "smalls" are in this work called "fines." The application of the Bessemer process to copper mattes is described in the last chapter. The process is pronounced as technically successful, but as useful only under certain conditions. The author's opinion is that the basic lining under present conditions would be of little use in the United States. The reason is that all arsenical or antimonial matte there produced is rich enough in the precious metals to warrant their extraction, during which operation the arsenic is eliminated.

It is interesting to learn that buyers often judge of coppers not by chemical or physical tests but by colour, a rose shade being accepted as the sign of a superior quality. Hence "dippings" have been devised for giving inferior samples this desired colour!

Metallurgists, and in general all persons interested in the copper trade, will find it advantageous to add this book to their library of reference.

Detection of Paraphenetidine in Phenacetine.—L. Reuter.—The author finds the reaction of the poisonous paraphenetidine with solution of iodine as less sensitive than that with chloral hydrate.—*Zeit. Anal. Chem.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiii., No. 24, December 14.

The Fixation of Nitrogen by Arable Soil.—Arm. Gautier and R. Drouin.—The authors, whilst admitting that atmospheric nitrogen is fixed, according to the researches of Th. Schloesing, jun., and E. Laurent (*Comptes Rendus*, vol. cxiii., p. 776), by the action of inferior green vegetation, especially chlorophyllic algæ, conclude from their previous experiments that the soil itself takes part in the process (see *Comptes Rendus*, vol. cxi., pp. 1174, 1233, and 1234). They argue that a small quantity of combined nitrogen is produced in the soil itself in virtue of its porosity, of its oxidisable organic matter, and of the aerobic microbia which provoke this oxidation. The preparatory absorption of the nitrogen by the microbia is doubtless one of the conditions of its oxidation. These organisms then give it up to the soil in the state of organic and amidic nitrogen. The algæ, the nitric and nitrous ferments, intervene in turn to fix these residues, but their intervention does not appear indispensable, as it is shown by the author's experiments, those especially in which neither algæ nor nitric ferments were present. By reducing the ammonia of the soil almost to nul, these latter organisms reproduce the conditions favourable to the action of the microbia which oxidise the humic matter and fix the nitrogen. Thus is explained at once the part of the humic matter, the utility of the ventilation and the cultivation of the soil, the non-assimilation of nitrogen in soils sterilised by heat or by antiseptics, as was observed long ago by M. Berthelot, and the influence of the superficial algæ. The soils containing organic matter, and such only, fix the free or the ammoniacal nitrogen of the atmosphere, even in the absence of plants, and the organic matter which exists in every arable soil is the indispensable medium for the formation of nitrogen.

Camphoric and Isocamphoric Ethers, and on the Constitution of the Camphoric Acids.—C. Friedel.—This lengthy paper is not adapted for useful abstraction.

Remarks on the History of Supersaturation.—Lecoq de Boisbaudran.—The author considers that supersaturation is a fact which is absolutely general, which is indispensable to crystallisation, and which accompanies all changes of state.

Three Basicities of Phosphoric Acid.—Daniel Berthelot.—Phosphoric acid is not a true tribasic acid, but rather a monobasic acid with complex functions. Its first function reminds us of that of the strong acids, its second of that of the weak acids, and its third that of phenol.

The State of Salts in Solutions: Sodium Sulphate and Strontium Chloride.—A. Etard.—The author has recently verified the conclusion that between 235° and 320° sodium sulphate follows a line of solubility which rapidly decreases, as it is shown graphically.

On a Green Solid Chromium Sesquisulphate.—A. Recoura.—The author finds that either on producing chromium sulphate in presence of a very small quantity of water, or by partially dehydrating by heat the crystalline violet sulphate, we obtain a new variety of chromium sulphate which is green, solid, and crystalline. It possesses properties quite distinct from those of the violet sulphate. M. Etard has also shown that if the solid violet sulphate is placed in contact with dehydrating liquids such as SO_4H_2 or NO_2H , it becomes green. But this is only a transient modification, for when the green sulphate thus obtained is freed from the dehydrating liquid it quickly returns to the violet condition.

On Bismuthic Acid.—G. André.—The author has formed and examined potassium bismuthate, and concludes that it is exceedingly difficult to obtain a bismuthic acid of constant composition. The combination of potassium with bismuthic acid is never complete and does not allow us to reach the composition of a neutral salt.

The Distillation of Coal.—Pierre Martin.—The author, at the instigation of the Société d'Encouragement, has executed analytical and calorimetric researches on fuels. In the present paper he gives his results with the coal of Commentry.

A Novel Porcelain: Asbestos Porcelain.—F. Garros.—The author has obtained a novel porcelain by grinding asbestos to an impalpable powder, removing iron, &c., if necessary, by treatment with hydrochloric acid, making the powder into a paste with water, and baking it in a porcelain furnace for 18 hours at 1200°. The porcelain thus produced may be used for the filtration and sterilisation of liquids. The experiments of Drs. Durand-Fardel and Bordas have proved that water containing 1200 colonies of microbes per c.c. are absolutely sterile after filtration through asbestos porcelain. At the same time it filters more rapidly than ordinary porcelain. Other comparative experiments made with the co-operation of MM. Cousin and Méran on the filtration of wines, vinegars, and acids, show that the porcelain may serve equally for the filtration and sterilisation of wines, vinegars, &c., and for the filtration of acids. (This invention must open out a new prospect for the asbestos districts of Canada).

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 4.

A Method for Conducting Elementary Analyses Electrothermically.—Johann Oser (*Kaiser. Akademie der Wissensch. in Wein. Math. Naturwiss. Classe*).—This paper does not admit of useful abstraction.

Method for the Volumetric Determination of Chloroform.—L. de Saint Martin.—(From *Comptes Rendus*, vol. cvi., p. 492).

Lead and its Sophistications.—H. W. Wiley.—(From "Foods and Food Adulterants,"—an investigation made by the Commissioners of Agriculture of the United States).

Geranium Oil.—Schimmel and Co.—This product is now largely sophisticated with fatty oils. This fraud can be detected by the behaviour of the sample with dilute alcohol. Pure geranium oil dissolves in 2–3 vols. of alcohol of 70 per cent (by volume) at 20°. If small quantities of fat are present the mixture is dull, or in case of larger quantities milky.

Detection of Chlorinised Compounds in Oil of Bitter Almonds.—Schimmel and Co.—The process given by the authors in *Zeit.* (vol. xxx., p. 90), is contested by Merck.

Impurity in the Pure Benzol of Commerce.—C. Liebermann and A. Seyenitz.—These authors (*Berichte Deuts. Chem. Gesell.*) state that this article contains considerable quantities of carbon disulphide, which appears to be a constant associate of coal-tar benzol. For its detection the authors add to 10 c.c. of benzol 4–5 drops of phenylhydrazine, and let the mixture stand from 60–90 minutes with frequent shaking. In presence of 0.2 per cent carbon disulphide there is formed a precipitate of phenylhydrazine phenylsulphocarbazinate which renders the liquid quite thick. The limit of the reaction is reached at 0.02 per cent (0.17 grm. per litre).

On Volumetric Determination of Hydrocarbon Vapours in Coal-Gas.—W. Hempel and L. M. Dennis (*Berichte Deuts. Chem. Gesell.*).—Already inserted.

Determinations of the Penta-Glycoses in Plants.—A. Günther and B. Tollens (*Ber. Deuts. Chem. Gesell.*).

—The author has operated on cherry-gum, wheat and oat straw, beech, and pine-wood. The first-mentioned material contains 45—46 per cent of arabinose.

Determination of the Specific Gravity of Blood, Alkapton Urine, Uroleucic Acid, Indigo Red in Urine, Hæmatoporphyrine.—For the detection of bile pigments in urine, and melanogenous substances in urine, we must refer to the original.

Detection of Mercury in Chémico-Judicial Investigations.—T. Lecco (*Berichte*).—The author shows that mercury is very sparingly soluble in hydrochloric acid and potassium chlorate, so that the reaction must be continued for hours after the organic substance is destroyed, applying heat and stirring.

Detection of Phosphorus Poisoning.—Th. Poleck. —Phosphorus acid was found by Blondlot's method three months after the death of the subject.

Detection of Cyanogen Compounds.—A. Hilger and K. Tamba.—The authors reject the use of the well-known copper sulphate and guaiacum papers. The substances are first mixed with tartaric acid, gradually rendered slightly alkaline with sodium carbonate, and then treated for some time at 60° (not higher) in a current of carbonic acid in a distillatory apparatus. The distillate is tested with the usual reagents for hydrocyanic acid.

Re-determination of the Atomic Weight of Glucium.—Gerhard Kruss and H. Moräht.—The atomic weight ($O=15.96$), appears to be 9.027, and the equivalent 4.5134.

Vol. xxx., Part 5.

Statistics of Wine-Production in Germany.—No. IV.—An elaborate report having no direct connection with analytical chemistry.

Contributions to the Characteristics of the Alkaline Earths and of Zinc Oxide.—Dr. G. Brugelmann.—The author originally used graphite crucibles for the preparation of baryta from barium hydroxide, as he expected that vessels of clay, porcelain, and platinum would be too strongly attacked. But even in crucibles of graphite it is impossible to obtain pure baryta from the hydrate, since, in addition to the ash of the fuel, they contain admixtures of clay, sand, &c. By the great rapidity of the decomposition, the absorption by the melting hydrate of material from the crucibles was much restricted, but not obviated. The "needles" in question were found not to be pure BaO, but a compound of this oxide with the materials of the crucible. They do not form a clear solution in water, but leave a considerable residue. The author has not examined whether this is a compound of baryta with alumina or silica, or both, or perhaps with other constituents of the crucible. What has just been said applies, though to a less extent, to the production of strontia and lime. Hence, whatever the author has formerly stated on the preparation of the alkaline earthy oxides from their hydrates and carbonates in other than platinum vessels must be deleted as non-valid, as also the figures given for the specific weight, the acicular form of baryta, the dimorphism of this oxide, and the suggested catalytic action of platinum. The author cannot confirm the assertion that strontium carbonate melts during its decomposition; it is merely fritted to a slight extent. The rapid and complete dehydration of barium hydroxide is effected only in the strongest white heat.

Support for Washing, Drying, and Absorbing-Tubes.—A. Gawalowski.—This paper requires the five accompanying cuts.

Separation of Baryta from Lime.—Professor R. Fresenius.—The author gives here a brief conspectus of the methods which he has discussed. 1. Complete separation of the two bases with perfectly satisfactory results: (a) separation by ammonium chromate with double precipitation; (b) separation by hydrofluosilicic acid, combined method. 2. Separation not quite perfect, but results

still satisfactory: (a) separation by ammonium chromate, single precipitation; (b) separation by hydrofluosilicic acid, elutriation process. 3. Separation still less complete, but satisfactory for moderate demands; results often apparently good from the mutual compensation of opposite errors: (a) separation by hydrofluosilicic acid, process hitherto general; (b) separation of the sulphates in mechanical admixture by sodium thiosulphate; (c) separation by sulphuric acid in a solution strongly acidified with hydrochloric acid; (d) separation by heating the sulphates with potassium carbonate; (f) separation by precipitation with a mixture of potassium carbonate and sulphate (Fleischer); (g) precipitation with ammonium sulphate and oxalate, and volumetric determination of the calcium oxalate. 4. Methods which must be pronounced as scarcely useful or quite worthless: (a) precipitation with sulphuric acid from a solution containing little hydrochloric acid; (b) separation of the mixed precipitate of sulphates by sodium thiosulphates; (c) separation by treating sulphates with ammonium carbonate; (d) separation by precipitation and digestion with a concentrated solution of ammonium sulphate.

Change of Volume on Mixing two Liquids, and its Influence on Refractive Power.—L. Buchkremer.—An Inaugural Dissertation. No particulars are given.

On Jamin's Interferential Refractor.—L. H. Siertsema.—An Inaugural Dissertation; no particulars.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Gas Compression.—A correspondent wishes to know of the address of a maker of apparatus for gas compression.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Medical, 8.30.

TUESDAY, 5th.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

Pathological, 8.30.

WEDNESDAY, 6th.—Geological, 8.

THURSDAY, 7th.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

FRIDAY, 8th.—Astronomical, 8.

SATURDAY, 9th.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

ERRATUM.—P. 319, col. 2, line 36 from top, for "grammatical" read "gravimetical."

THE CHEMICAL NEWS

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THE CHEMICAL NEWS.

VOL. LXV., No. 1676.

THE DENSITY OF SULPHURIC ACID SOLUTION.

By G. LUNGE.

IN the CHEMICAL NEWS (vol. lxiv., p. 311) Prof. Pickering replies to my remarks on the relative accuracy of his and my specific gravity determinations of sulphuric acid. Those remarks had been called forth by a paper (*Journ. Soc. Chem. Ind.*, 1890, p. 479), in which Mr. H. D. Richmond—after comparing some of Prof. Pickering's figures with those formerly obtained by Naef and myself, by Winkler and by Archbutt—came to the conclusion that Prof. Pickering's determinations were preferable to all others. From these he has constructed a specific gravity table for sulphuric acid, which he gives to the world as the most accurate in existence, and as such Mr. Richmond's table has been reprinted in other publications. As I had previously published a very elaborate table of the same kind, based on the work of myself and my collaborators Naef and Isler; as I, rightly or wrongly, believed, and still believe, that *our* estimations are the most accurate hitherto made; as I, moreover, felt constrained to give my reason why I did not accept Mr. Richmond's table for the new edition of the "Alkali Makers' Pocket-Book," which was then in course of preparation, I felt bound to show why Prof. Pickering's results, in spite of the "seemingly stupendous accuracy of his observations," were not to be preferred to mine.

I do not know what more legitimate reasons for exercising criticism could have existed than those which I have stated. Prof. Pickering, however, sees fit to call this "feeling hurt, apparently, that anyone else's determinations should have been preferred to my own." It is useless to discuss the good taste of this imputation, as it is only a trifle in comparison with what follows. "Gross misrepresentations," "bold statements," "blunders made by critics who decline to read the papers which they attempt to criticise," "self-restraint on my part not to accuse the critic of a wilful misrepresentation of statements and a perversion of the facts of the case," "misrepresentations so glaring that it seems scarcely possible to attribute them to mere carelessness on his part," "ridiculous,"—these are some of the words thrown at my head. Prof. Pickering is not content with rectifying any misunderstanding which I may have committed, but he charges me with uttering deliberate falsehoods in order to calumniate him. That he covers this charge with an extremely transparent veil, barely sufficient to avoid the risk of an action for libel, I disdain to notice. But I disdain just as much to answer such a charge, which cannot but rebound upon him who has made it. Prof. Pickering does not even give me the traditional choice between knave and fool; I must needs be both in an egregious degree. He represents me as committing the incredible stupidity of wilfully calumniating him in one of the most widely circulating English chemical journals, and in a book which I must desire to be read by as many chemists as possible, with the absolute certainty of immediately encountering the phials of his wrath. I have now been before the chemical public as an author and leader for thirty-two years, and I am personally known to most of the leading English chemists; I leave it confidently to them to judge whether Prof. Pickering's accusations against me, of wilful mis-statements, is within the range of possibility or not, and I shall confine myself to answer him as if he had merely charged me with misunderstanding him. I believe that I have done so in minor points, and that I am right in the principal issue.

Prof. Pickering seems to have forgotten that hard words do not amount to *arguments*, and are generally held to show that he who uses them in a violent manner feels touched in a sore part. If I wished to use the same weapons as my antagonist, I should perhaps say that he expected extremely few of your readers would wade through the dreary wilderness of figures in his paper on Sulphuric Acid, in order to control his corrections of my alleged misrepresentations. I will not, however, follow him in the way of imputations, and merely state *facts*.

Professor Pickering implies that I ought to have taken notice of his reply to Mr. Sidney Lupton's strictures on his paper; and yet he must know that my remarks were in print many months before the controversy happened between himself and Mr. Lupton and other adversaries.

The principal point at issue between us (for I shall certainly not waste your space over the other accusations of "carelessness," which are trifles to anybody else, and are in no case of any importance at the place where they stand) is this: that I am accused of having imputed to Prof. Pickering to have claimed that the percentages of his acids are accurately known to the third decimal per cent, whilst the analyses of his acids made by Mr. Compton varied between 99.704 and 99.962 per cent. Prof. Pickering maintains that he did not rely on Mr. Compton's analyses for determining the strengths of his acids, but that he found and accepted a method more reliable than any analysis, based on the fact that the pure acid must have a higher freezing-point than any acid with excess of either water or anhydride. But in his paper, after having given Mr. Compton's analyses, and the mean value he deduces from them, and then, having mentioned his own new method, he continues (p. 73, line 5 to 10): "As all the present results had been calculated out long before this later work had afforded this more certain means of ascertaining the strength of the acid, and as the error would not appreciably affect these results when differentiated, I did not think it worth while to alter them, except in a few cases where the introduction of the correction will be specially mentioned." If that does not mean that all his results (excepting those "few cases") were based upon Mr. Compton's analyses, then I do not understand the meaning of English words.

On the same page Prof. Pickering describes his methods for diluting the strong acid. Employing quantities of 100 to 200 grms., and using a balance reading to 0.0001 grm., he maintains that their relative composition is accurately known to "about one unit in the fourth decimal place of the percentage." If a magnitude is known to "about one unit" of the fourth decimal, it is *accurate* to the third decimal, as I put it, and I fail to see in this case either carelessness or misrepresentation on my part. Now it is true that Prof. Pickering here uses the expression "relative composition," and I am so far in fault that I omitted to notice the word "relative." But I would defy most readers, wading through Prof. Pickering's 124 pages, and tens of thousands of figures, to bear it always in mind that all those figures refer, not to real percentages, but to "relative compositions." So much is certain, that Mr. Richmond does not mention this either, but takes Prof. Pickering's tables as representing *absolute* values; on any other basis his calculating therefrom another table for practical use would have been absurd and directly misleading. But he had evidently, like myself, taken the values as absolutely given. If Prof. Pickering claims for them only a *relative* accuracy, for differentiating purposes; they are useless for constructing practically workable tables, and I will not start a new dispute by pointing out that the limit of accuracy of the balance is far from exhausting the possible sources of error in such determinations, not even when adding his *contradictio in adjecto*, "provided no loss of anhydride occurred in making them" (the dilute acids).

Whether Prof. Pickering's new physical method for estimating the strength of sulphuric acid is really, as he believes, superior to any analytical method, I will not

stop to discuss. But I may be allowed to submit that, in my humble opinion, the great majority of chemists will, for all practical purposes, prefer a specific gravity table founded upon a basis which they all understand and can check for themselves, namely, the most accurate analytical method known, to a table founded upon the hypothetical basis that the pure hydrate must have the lowest freezing point, and adding water to this. Nor will, probably, the differentiation of the contractions by Prof. Pickering be very convincing to most people. So long as there exists such great uncertainty about the nature and properties of solutions and the hydrates contained therein, any mere paper work, founded upon differentiations of contractions, confers no right of saddling a practical observer with the blame of inaccuracy. Before such a blame can be held to be substantiated, evidence more directly appealing to chemists must come forward.

It is, perhaps, no matter of surprise that the various strong attacks made upon his laborious work on solutions have put Prof. Pickering out of temper. That does not, however, entitle him to neglect, in scientific controversy, all ordinary rules, not merely of courtesy, but of common fairness. I think I shall hence be held justified if I decline any further discussion with an antagonist who "hits below the belt."

THE CONTRACTION ON MIXING SULPHURIC ACID AND WATER.

By SPENCER U. PICKERING, F.R.S.

IN a communication on the densities of sulphuric acid solutions (CHEMICAL NEWS, vol. lxi., p. 312), there appeared a sentence which I had erased in the proof, but which was accidentally allowed to remain in the text: it was to the effect that it had been known for some time that the maximum contraction occurring when the acid is mixed with water is situated at different strengths according to the temperature. This statement referred to the contraction calculated per unit weight of the solution formed, and rested on the authority of Mendeleeff, who had not any very complete sets of determinations at his disposal when he deduced this conclusion (*Ber. Deut. Chem. Gesell.*, 1886, p. 387), and, on second thoughts, I considered it advisable not to repeat it before I had ascertained whether my own determinations (*Chem. Soc. Trans.*, 1890, pp. 139—144) led to similar results. These determinations I have now examined, and find that they do show the point of maximum contraction per unit weight to shift with the temperature, but that the point of maximum contraction per unit volume of solution formed is practically unaltered by temperature. This statement refers to a range of temperature from 8°—38°.

The following table contains the results. All the percentages have been corrected in accordance with the later and more accurate determinations of the strength of the acid used by me (*vide loc. cit.*, p. 73), and a very small correction has been applied to the densities at 17°925°, to correct for the error mentioned on page 72 of my communication.

On plotting out the values for the contractions per unit weight, and drawing a smoothed curve through them, the following are found to be the positions of the maximum:

At 38°203° it is at 70.1 per cent, and = 0.059907
 " 28°064° " 69.1 " " 0.061040
 " 17°925° " 67.5 " " 0.061825
 " 7°978° " 67.0 " " 0.062827

These values show an undoubted shifting of the maximum towards the stronger solutions as the temperature rises, but whether this shifting occurs at a regular rate or not cannot well be determined owing to the gradual manner in which the maximum is reached, and the consequent difficulty in determining its exact position.

The values for the maximum per unit volume are as follows:—

At 38°203° max. at 76.3 per cent, and = 0.097957
 " 28°064° " 76.0 " " 0.100010
 " 17°925° " 76.0 " " 0.101585
 " 7°978° " 75.8 " " 0.103595

A slight shifting in the same direction is shown by these numbers, but as it is considerably within the limits of experimental error this maximum must be said to be practically unaltered in position.

It will be noticed that the position of neither of these maxima agree with the composition of the dihydrate, which contains 73.14 per cent of acid, nor with any of

Contraction on Mixing Sulphuric Acid with Water at 38°203°.

Acid p.c.	Density.	Volume.	Volume of components.	Contraction per gram.	Contraction per c.c.
100	1.813643	0.551376	—	—	—
79.9112	1.707359	0.585700	0.642390	0.056690	0.096790
78.9338	1.696495	0.589451	0.646816	0.057365	0.097320
77.8920	1.684849	0.593525	0.651537	0.058012	0.097742
75.8532	1.661610	0.601826	0.660773	0.058947	0.097947
73.9337	1.639397	0.609981	0.669461	0.059480	0.097511
71.9710	1.616740	0.618529	0.678352	0.059823	0.096710
69.8816	1.592543	0.627927	0.687829	0.059902	0.095397
67.9601	1.570547	0.636719	0.696534	0.059315	0.093942
65.9782	1.548091	0.645358	0.705512	0.059554	0.092195
63.9998	1.525956	0.655327	0.714476	0.059149	0.090256
0	0.993070	1.006978	—	—	—

At 28°064°.

100	1.823805	0.548304	—	—	—
79.9112	1.717424	0.582268	0.639780	0.057512	0.098773
78.9338	1.706389	0.586033	0.644230	0.058197	0.099307
77.8920	1.694596	0.590111	0.648974	0.058863	0.099749
75.8532	1.671094	0.598411	0.658258	0.059847	0.100010
73.9337	1.648712	0.606534	0.666999	0.060465	0.099689
71.9710	1.625844	0.615065	0.675926	0.060861	0.098951
69.8816	1.601168	0.624428	0.685450	0.061022	0.097725
67.9601	1.579326	0.633182	0.694200	0.061018	0.096367
65.9782	1.556737	0.642369	0.703225	0.060856	0.094737
63.9998	1.534480	0.651687	0.712227	0.060540	0.092897
0	0.996353	1.003660	—	—	—

At 17°925°.

100	1.833937	0.545275	—	—	—
79.9279	1.727959	0.578717	0.636806	0.058089	0.100380
78.9338	1.716617	0.582541	0.641340	0.058799	0.100936
77.8989	1.708215	0.585407	0.644691	0.059284	0.101270
75.9030	1.681394	0.594745	0.655161	0.060416	0.101583
73.9517	1.658444	0.602074	0.664059	0.061085	0.101306
71.9714	1.635125	0.611574	0.673089	0.061515	0.100585
70.0480	1.612588	0.620121	0.681850	0.061729	0.099544
68.0530	1.589441	0.629152	0.690958	0.061806	0.098237
66.0860	1.566869	0.638215	0.699927	0.061712	0.096695
64.8448	1.552820	0.643990	0.705588	0.061598	0.095651
64.0663	1.543990	0.647673	0.709137	0.061464	0.094900
0	0.998712	1.001293	—	—	—

At 7°978°.

100	1.844263	0.542222	—	—	—
79.9112	1.738076	0.575349	0.634206	0.058857	0.102298
78.9338	1.726694	0.579142	0.638681	0.059539	0.102806
77.8920	1.714570	0.583237	0.643452	0.060215	0.103243
75.8532	1.690580	0.591512	0.652788	0.061276	0.103592
73.9337	1.667782	0.599599	0.661577	0.061978	0.103366
71.9710	1.644541	0.608072	0.670554	0.062482	0.102754
69.8816	1.619860	0.617352	0.680130	0.062778	0.101713
67.9601	1.597410	0.626013	0.689929	0.062916	0.100503
65.9782	1.574588	0.635087	0.698003	0.062916	0.099067
63.9998	1.552015	0.644324	0.707063	0.062739	0.097372
0	0.999890	1.000110	—	—	—

the hydrates the existence of which I inferred from breaks in the curves representing various properties of the solutions, and it is scarcely necessary for me to point out again that a maximum point by no means necessarily coincides with a change of curvature. Prof. Lunge's statement that the maximum does coincide with the dihydrate, and also Mendeleeff's statement to the same effect ("Principles of Chemistry," vol. ii., 237), cannot, therefore, be accepted as correct.

An interesting point may be noticed respecting the contraction, namely, that the effect of temperature upon its value does not vary in any very simple or apparently regular manner with the temperature. Thus, taking the amount of contraction per unit volume occurring at the maximum (76 per cent), this amount increases at the rate of 0.000203 per degree from 38°—28°, at the rate of 0.000155 from 28°—18°, and at the rate of 0.000202 from 18°—8°, the rate for both the extreme temperature intervals being much greater than that for the intermediate interval. The irregularity is far too great to be attributed to any experimental error, for it would require errors twenty or thirty times greater than the known experimental errors, to reduce these three rates so as to bear any simple relation to the actual temperatures, and, moreover, the seeming irregularity occurs not only with solutions of one particular strength, but throughout the whole range over which the present calculations extend: thus with 64 and 80 per cent solutions the following rates of increase of contraction occur:—

	64 per cent.	80 per cent.
38°—28° ..	0.000260 per deg.	0.000193 per deg.
28°—18° ..	0.000191 ..	0.000161 ..
18°—8° ..	0.000254 ..	0.000194 ..

ON THE ACTION OF HEAT ON SOLUTIONS OF SALTS OF CHROMIUM.

By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

It has long been known that there are two kinds of chromium salts capable of existing in solutions, namely the red, violet, or blue, and the green modifications. The difference in constitution between the green and the other salts of chromium was in part the subject of researches made by me in the year 1872-74. A preliminary notice was published in the *Proceedings* of the Royal Society, vol. xxii., p. 241; and a full account of the work was submitted to the Royal Society at a later date, together with a brief extract, entitled, "On the Action of Heat on the Absorption Spectra and Chemical Constitution of Saline Solutions." This appeared in the *Proceedings*, vol. xxxiii., p. 372, 1875.

It contains the following paragraph:—"The action of heat on the violet hydrated compounds of chromium is not simply a dissociation of water molecules, or of acid from base, but a true decomposition, resulting in the production of a different class of salts with different generic properties.

The publication of the paper in full was postponed for the completion of certain physical measurements which would have increased its interest, but, owing to the fact that at the time it became impossible to execute this additional work, the entire paper has never been printed.

The general conclusions derived from the spectroscopic examination and determination of the chemical constitution of a large number of salts, some of which were rare and others entirely new, were in no way affected by the omission of the details to which I refer.

The most complete, though still inadequate, record of this work is contained in the *Proceedings* of the Royal Institution, for 1875, being the report of a Friday evening discourse delivered on April 30th, to a portion of which

additional interest is lent at the present time on account of a recent thermo-chemical investigation of M. A. Recoura, on the action of heat on solutions of chromic oxide (*Comptes Rendus*, cxli., p. 1439).

It was shown that green solutions of chromium, having the same absorption spectrum, may be produced from the sulphate or nitrate by the three following methods:—(1) By boiling a solution of the purple salt; (2) By dissolving an excess of the bluish chromic hydrate in the purple solution; (3) By neutralising with an alkali one-third of the acid in a solution of the purple salts.

If 50 c.c. of a solution of the sulphate or nitrate be boiled so as to form the green salt, it will not yield a precipitate if diluted with two or three litres of water and further boiled; but when one-third of the acid present has been previously neutralised, or when an excess of chromic hydrate is dissolved in the blue solution, a basic salt is thrown down on boiling with much water. This is exactly the behaviour characteristic of a salt described by Schrötter, to which he assigned the formula $\text{Cr}_2\text{O}_3 \cdot 2\text{SO}_3$, which may be written $\text{Cr}_2\text{O} \cdot 2\text{SO}_4$. Löwel has described a chloride, which is formed at 100° C.; this he formulates thus:— $\text{Cr}_2\text{O}_3 \cdot 4\text{HCl}$, and the formula may be modified in the following manner, $\text{Cr}_2\text{O} \cdot \text{Cl}_4 \cdot 2\text{H}_2\text{O}$. The constitution thus modified has the recommendation that it explains the decomposition of the substance when heated to a high temperature, which Löwel's formula does not. At or about 300° C. the compound is resolved into a mixture of the anhydrous violet chloride, CrCl_3 or Cr_2Cl_6 , and the anhydrous green oxide, Cr_2O_3 . If the original salt were merely a combination of the chromic oxide with hydrochloric acid, heating would drive off the volatile acid and leave the oxide only, but the actual change indicates that the chromium and chlorine are in direct combination.

Hence the conclusion that the effect of heat on the purple chromium solutions is not traceable to dehydration, but to a well-defined chemical reaction which yields a distinct class of compounds.

The violet or purple compounds of chromium have the general formula $\text{Cr}'''\text{R}_3 \cdot x\text{H}_2\text{O}$, or $\text{Cr}''''\text{R}''_3 \cdot x\text{H}_2\text{O}$, where R is Cl or NO_3 and R' is SO_4 , or the like.

When solutions of these are heated to 100° C. there is formed a class of substances which may be written thus: $\text{Cr}'''\text{OR}_4 \cdot x\text{H}_2\text{O}$, and $\text{Cr}'''\text{OR}''_2 \cdot x\text{H}_2\text{O}$, or the first compounds may be said to contain Cr''' as the base, while the second contains the radical $\text{Cr}'''\text{O}$. This tetrad radicle I proposed to term *chromyl*, just as UO is called *uranyl*.

The conclusions of M. Recoura are to the effect that when a purple solution of chromium sulphate has been converted into the green modification by boiling, exactly half an equivalent of free H_2SO_4 exists for each $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3$ from which it has been derived.

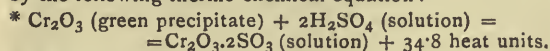
It thus appears that the basic green salt formed by the action of heat on a normal solution of chromic sulphate, has the definite composition of $2\text{Cr}_2\text{O}_3 \cdot 5\text{SO}_3$, and that it contains a modified form of chromic oxide which, definite experiments showed, is incapable of combining with more acid than the formula above indicates.

The following is the mode of operating in order to arrive at this conclusion. A solution of the sulphate which has been converted from the purple to the green condition by boiling is mixed with an exactly-measured quantity of soda solution, and the heat evolved is measured. If the heat evolved be in accordance with that liberated by free sulphuric acid, under the same conditions of dilution, namely 31.2 heat units for every proportion represented by Na_2O , it may be concluded that the soda has not decomposed the chromium salt, but simply neutralised an equivalent quantity of free acid.

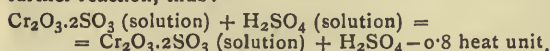
To verify this result a quantity of sulphuric acid equivalent to the quantity of soda previously used is added to the solution. By this means it was ascertained that there was no evolution of heat, but, on the contrary, a slight heat absorption equivalent to 0.2 heat units for Na_2SO_4 , which, M. Recoura mentions, is due to

the action of the free acid upon the sodium sulphate. But when an excess of soda amounting to no more than 1-20th an equivalent beyond that necessary to neutralise the free sulphuric acid was used, the subsequent addition of acid caused heat evolution, which arose from the action of the acid upon the chromium hydrate set free by the 1-20th Na_2O (+0.6 heat unit).

It is admitted that the salt $2\text{Cr}_2\text{O}_3 \cdot 5\text{SO}_3$ contained in solution does not yield an oxide or hydrate capable of the same degree of saturation as that indicated in this formula, for when the base is precipitated by an alkali it combines with only two molecules of H_2SO_4 , as shown by the following thermo-chemical equation:—



If another molecule of acid be added, there is no further reaction, thus:—



As this reaction is feebly endothermic, there is evidently no further combination of the acid with base or with the basic sulphate. M. Recoura therefore concludes that the salt in solution is $2\text{Cr}_2\text{O}_3 \cdot 5\text{SO}_3$, but that the salt formed by the action of sulphuric acid on the green precipitated hydrate, obtained from this solution, is $\text{Cr}_2\text{O}_3 \cdot 2\text{SO}_3$. He states that "the oxide precipitated is a new modified oxide of which one molecule fixes only two molecules of sulphuric acid."

Not only, therefore, are the conclusions as to the existence of this oxide and a new class of salts, as described in the *Proceedings of the Royal Institution*, confirmed, but M. Recoura's work also demonstrates the existence of two green sulphates with different compositions, as stated above, and thus affords an explanation of the difference in behaviour of dilute solutions of these salts when boiled. The empirical formulæ determined may very inadequately represent the constitution of the salts in these solutions, for they are almost certainly hydrated salts.

ON THE DETERMINATION OF THE MELTING POINTS OF MINERALS.†

PART I.—THE USES OF THE MELDOMETER.

By J. JOLY, M.A., D.Sc., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

(Continued from p. 3).

Sublimation on the Meldometer.

ALTHOUGH the majority of mineral bodies have melting-points ranging over 900°C. , some, such as the sulphides, arsenides, and some of the elements, can even be brought into the state of vapour upon the meldometer. When this is the case we find that this apparatus affords a means of obtaining sublimates much transcending the blowpipe (used either with carbon or aluminium) in delicacy, range, and purity. Sublimates may, in fact, easily be obtained from substances which treated in the blowpipe would appear to afford none, as will appear. The mode of procedure is as follows:—A circular cover-glass,

not too thin, grasped in a forceps, is held horizontally above the platinum ribbon, as the temperature is being raised. If the sublimate is one which oxidises, we obtain the oxidised sublimate alone; or the unoxidised sublimate bordered by the oxide, according as we hold the glass further or nearer to the ribbon.

The more volatile elements often afford as sublimates both the element and an oxide of it. The elemental sublimate may often be obtained nearly pure by suitably regulating the temperature. Thus, at low temperatures, arsenic sublimes as a rich grey-black sublimate, showing the mirror when viewed through the glass. At a higher temperature, especially if the glass is held at a distance of 3 or 4 c.m. above the ribbon, the white oxide—the trioxide—only is obtained. Sometimes both element and oxide are together on the one glass, affording an "eye," the pupil of which is the element. This results from the screening action of the outer parts of the ascending column of vapour, the central parts being, in fact, sublimed in the absence of oxygen, which is all absorbed in the outer layers of the vapour. Magnesium affords similar eyes surrounded by the white oxide, or in many cases veiled over by it, so that the dark metal is only seen through the glass. The great avidity of this element for oxygen is shown in this fact. Tin also affords "eyes." Thallium throws a rich black velvety sublimate, fringed with deep ash-red (the oxide?). This is a very beautiful sublimate, but very fleeting, the black soon fading into a pale greyish-brown colour. If immediately enclosed from the air it retains its original tints a longer time. Cadmium may also be sublimed as the metal and its oxide. Indium affords a white sublimate, dashed with pink and yellow.

While the metal is thus sometimes obtained with the oxide, it more generally affords the oxide only. This is the case, so far as I have observed, with vanadium, lead, wolfram, bismuth, tellurium, zinc, and antimony. But, again, sometimes the element appears to sublime without oxidising. Thus silver affords a grey-black veil of the metal, iridescent where thinly deposited. Gold is also sublimed. Sulphur is another case, the oxide being a gas at atmospheric temperatures. Mercury gives a sublimate of a grey colour, consisting of globules of the element.

As regards compounds, the command we have over the temperature in the meldometer enables many very distinct separations to be effected. Thus, dealing with realgar, at low temperatures, the substance is sublimed unaltered in a rich yellow sublimate. Somewhat higher a decomposition is effected, the free arsenic showing as a white sublimate of the oxide round a yellow eye of sublimed realgar. As the temperature rises the effect is more and more that proper to arsenic only, the liberated sulphur not appearing; but the eyes remain most generally distinctly touched with realgar. Orpiment behaves in a similar manner. Pyrargyrite, a compound of silver and antimony sulphides, throws off the antimony first in a rich white sublimate of the oxide, touched more or less with a pale pink cloud, probably the unaltered compound. A bead of silver is left upon the ribbon, which ultimately volatilises to the grey-black sublimate of silver. Clausthalite, the selenite of lead, affords first a sublimate of selenium, a fine ash-red; this then becomes veiled over and intermixed with the rich yellow and whites of the lead oxides, so that a very beautiful marbling is produced, which shows stronger tints of red seen from the back of the glass than from the front.

Many such effects are seen in a similar order with the blowpipe, but are not produced with the ease, certainty, and cleanliness obtaining with the meldometer. Tests may very conveniently be applied to these sublimates as they repose upon the glass, in the knowledge that the only addition to the original substance can be oxygen. Sublimates also may be obtained from very minute quantities of the substance. This is an advantage in more ways than one. Many of the bodies mentioned above—as arsenic, tin, zinc, bismuth—attack the platinum ribbon

* It may be remarked that in the above equations, where $O=16$, the heat units evolved are + 34.8, while for $O=8$ the number is of course one half or + 17.4, as in the original publication. An error occurs in the abstract of this paper in the *Journ. Soc. Chem. Ind.*, vol. x., p. 925, for the symbols are written with $O=16$, and the thermal values with $O=8$. The liability to mistakes which arises from the conversion of equivalent into atomic formulæ would be lessened by quoting thermal equations exactly as written, whether they be additionally translated into atomic formulæ or not.

† A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

at high temperatures, and cut it if more than a very small quantity be used. The metals iron, gold, and silver again amalgamate with it. If it is desired, however, to obtain considerable quantities of the sublimates of the more volatile elements, it is possible by laying upon the ribbon a small slip of thin mica, and upon this the substance, to volatilise considerable quantities of it. Lest it be urged that this apparatus is an expensive one to use, owing to the necessity of using platinum, I may mention that a spool of the pure platinum ribbon, having a length of 1700 c.m. wound upon it, is supplied to me by Messrs. Johnson and Matthey, of Hatton Garden, London, at a cost of twenty shillings. This lasts an indefinite time, as a couple of centimetres serves most generally for many observations, and in the case of silicates may then often be cleaned, so as to be again serviceable, by treatment in acids. That the platinum, however, volatilises slowly at high temperature is shown by the fact that if fragments of quartz be heated upon it nearly to their melting-point, they will be found to become covered with minute crystals of platinum upon their upper surface (see *Nature*, xlv., 1891, p. 124).

But the maldometer is capable of affording sublimates which the blowpipe very certainly will not reveal. Thus, for example, *tourmaline* affords a pale whitish-yellow sublimate, the nature of which I have not determined; and *enstatite* volatilises at the highest temperatures obtainable, very nearly, giving a pale brown sublimate. An addition may be made to this form of the maldometer, which will permit of sublimates being obtained in the absence of free oxygen. This is an annular chamber of light brass open at both sides, and cut into at two points, so that it can be set down upon the base plate of the maldometer, the two slots admitting the forceps without making contact with them. It is provided with two small projections which, entering perforations in the base plate, retain it in position. It is shown dotted in fig. 1. Across the upper surface of this box the cover-glass to receive the sublimate is placed, and the sublimate thrown upon it in the usual manner. A tubular at one side permits of connexion with a supply of CO₂ or other gas, which, flowing in very slowly under slight pressure, and escaping around the forceps, replaces the air and stops its entry. If the sublimate is a very heavy one—that is, one which falls downward when generated—a second, smaller, cover-glass is supported above the floor of the chamber upon a little tripod twisted out of wire, so as to be just beneath the forceps. In this way sublimates of realgar and arsenic may be made to afford the unoxidised substances. As it is necessary, in order to obtain an abundant sublimate, that there should only be a slow motion of the atmosphere around the platinum, guards are arranged, attached to the base plate beneath the forceps, which close the slots provided in the ring when this is in its place. It is further well to loosely close the opening between the limbs of the forceps with a little cotton-wool. A very slow current of inert gas then effectually secures that no air enters while the sublimate is being taken. However, in the use of this arrangement, the sublimate is generally obtained deposited in patterns—often very regular—upon the glass, due to slow swirling currents within the chamber.

Pyro-Chemistry on the Maldometer.

Before passing from the subject of the secondary uses to which this form of the maldometer may be put, it remains to add that much of the pyro-chemical work done with the blowpipe may with greater ease and delicacy be effected upon the maldometer. Thus, glasses with microcosmic salt or with borax may be made readily upon the ribbon, the colours produced being well seen, and that, too, however deep in tint, where they thin out at the ends along the bright platinum strip.

Again, abandoning the use of the ribbon, we may substitute a platinum wire carrying a loop at its centre, and, clamping it in the forceps, form beads of the usual form

from the action of the hot wire. These may be observed, under the microscope, while hot. Changes of colour, often so characteristic, are very distinctly observed through the microscope, directed upon the platinum ribbon. For example, the changes of tint of a glass formed of copper oxide (CuO) with borax, coating the ribbon, as the temperature is slowly raised, is from a fine blue through every gradation of tint to a greenish-yellow. The command we possess over the temperature enables these successive changes to be very readily observed. Similarly, the oxidising effects of the blowpipe may be obtained by addition of oxidising substances, such as potassium nitrate. Thus, as with the blowpipe, a glass formed of the sesquioxide of cerium and microcosmic salt, which is a pale yellow when hot, passing to colourless when cold, may, by the addition of KNO₃, be intensified to a vivid yellow when hot, to colourless when cold. By the use of reducing agents deoxidation may, of course, be effected. In this way a mixture of cupric oxide with carbonate of soda and cyanide of potassium yields, first the lower cuprous oxide as a transparent red crystalline body, and finally the metal which alloys with the platinum. The most minute quantities may be used. I have not had leisure to develop this application of the maldometer, but would call the attention of those versed in pyro-chemistry to the facilities it offers for minute and clean work. The form now described possesses the added advantage that the temperature at which any phenomenon is occurring can be determined with as much facility as we read a thermometer.

Measurement of Temperature on the Maldometer.

The temperature of a homogeneous conductor of constant section, heated by the passage of a current, may be considered uniform throughout; the same at the centre of section as at the surface. The difference is measured probably by hundreds of a degree only. Prof. Heinrich Streintz has calculated (*Pogg. Ann. der Phys. und Chem.*, clx., 409) the temperature difference in certain cases, and it appears that for the present purposes it is certainly unnecessary to take it into consideration.* It is allowable further to assume that a fine dust resting upon the surface of a flat conductor, such as is used in the maldometer, is very closely at the temperature of the conductor, especially when near the central line, where, surrounded by neighbouring particles, it is sheltered from draught. It is, indeed, true that for the accuracy of the measurements made on the maldometer it is not necessary to assume that the agreement in temperature should be exact, as will be seen, but only that the difference should be about the same from one substance to another. The point here is that the difference being in any case very small there cannot be much diversity in the temperature difference between substance and platinum from one case to another. Assuming, then, that the average temperature throughout the cross section of the wire is that of its surface, and that the finer dust resting upon this surface is nearly at its temperature, it only remains to measure the temperature of the platinum ribbon in order to determine the temperature of the substance.

First attempts in this direction were directed at determining the temperature in terms of the electrical resistance, a well-known formula of Siemens's being used to express the relation between the two.

In these experiments the ribbon used was 6 to 8 c.m. in length, and the following temperatures of slow softening were determined:—

Adularia	865° C.
Garnet, dark red ..	972 "
Beryl, clear green ..	882 "
Actinolite, dark green	971 "

Beryl was observed to be a very viscous body, apparently even more so than adularia. Garnet and actinolite,

* If, however, the ribbon of platinum be raised nearly to its melting-point, it will be found that signs of fusion appear first along the central line.

on the other hand, were found to melt with comparative suddenness. Diallage behaves much as actinolite. Natrolite whitens and decrepitates before fusion. The softening temperatures of these latter minerals were not determined; but, by comparison, the specimen of diallage used was found to melt at a slightly higher temperature than the actinolite. In these experiments the platinum ribbon was enclosed in a long narrow box of platinum foil provided with a lid, through a hole in which observations were made at intervals, the hole being covered between times. The softening point was sought by prolonged exposures (up to twenty minutes) of the substance in a state of fine dust to a particular temperature of the ribbon. It has been already pointed out that at much less expenditure of time, by a somewhat different procedure, the incipient softening of viscous substances may be detected.

Subsequently Mr. Callendar (*Phil. Trans. R. S.*, clxxviii., 161) compared the readings of the air-thermometer and the platinum resistance thermometer up to 600° C. However, notwithstanding the help thus afforded, the cumbersome apparatus and tedious measurements required in the case of the maldometer, in which the resistance has to be determined while a current is traversing the circuit, rendered the method inapplicable. It was accordingly abandoned after much labour had been spent upon it, and, at a later date, the present form of maldometer devised, which depends on the thermal expansion of the ribbon for the estimation of temperature. The general mode of procedure in the present method is as follows:—Using a much longer ribbon than that previously described, we determine its increase of length (by a contrivance to be described) when a salt of known high melting-point is seen to melt upon its surface, and again when two or more other substances, differing from each other in melting-point as much as possible, are melting. This is analogous to determining the fixed points on a thermometer, and assumes, as in the latter case, nothing as to the absolute coefficient of expansion of the working substance. Thus, if we read the movement of the mercury in a thermometer when we raise it from the known temperature of melting ice to the known temperature of boiling water, we may evidently, on the assumption of the uniformity of the expansion of the mercury between the two points and of the uniformity of the bore, estimate the temperature of any intermediate reading, using a system of numbering decided upon beforehand. Similarly the assumption is made in the case of the maldometer that there is uniformity of expansion over the limits of known temperature, and for some distance beyond them. In fact, in this method, we take advantage of the experimental work of past observers. Much of this, more especially that of Carnelley and Violle, is very careful. It is sufficient to determine five or six points at various intervals along the scale, and plot the extensions corresponding as ordinates along any uniformly divided line serving as a scale of temperatures. The points so determined are joined by a line which will be found very slightly curved over its lower length, in which we use the experiments of Carnelley. In the upper range—from 900° to 1500° C.—we have very careful data of Violle's, which plot as a line of slowly increasing curvature, convex to the axis of temperature, and meeting tangentially the range covered by Carnelley's experiments. To determine now the melting-point of an unknown substance, we obtain the extension corresponding to its point of melting and scale from the chart the temperature proper to this extension. This is all that is required to determine the melting-points of minerals to the degree of accuracy attained in the elaborate researches of Carnelley and Violle. Although the extensions, as determined directly, may be thus used to determine unknown temperatures, it is preferable to plot in each case the ratio of the extension to the original length of the ribbon, or the quantity $l_2 - l_1/l_1$, this value being independent of the length of ribbon used in making the experiments, a length which it is inconvenient to

regulate to uniformity on all occasions. The value of this fraction is certainly applicable to all observations made with platinum of the one quality, or to the contents of the one reel if certain precautions be taken which will be described later. In this way a curve once plotted may be kept in use for many observations. The chart accompanying this paper is plotted in this manner.

(To be continued.)

AN ALLOY OF TIN AND SODIUM WITH A DEFINITE COMPOSITION.

By HENRY BAILEY.

In a recent endeavour to prepare an allotropic modification of tin by acting on its sodium alloy with water, I was struck by the uniformity in appearance and behaviour of several of my alloys to which an excess of sodium had been added, and which had been subjected for a considerable time to a high temperature. A quantity of this substance was prepared by mixing together tin and sodium (the sodium being in excess) in a crucible provided with a luted lid, through which a small hole had been drilled so as to allow the excess of sodium to escape as vapour. Air was excluded by means of a lump of charcoal being placed loosely over the hole. The crucible and its contents were then heated for a considerable time until it was judged that all sodium existing as such was volatilised. After cooling in an inert atmosphere, the content of the crucible was extracted, and was found to consist of a very brittle mass externally covered with a slight white scoria, which on fracture revealed brilliant crystalline, in fact almost crystallised facets, of a beautiful bronze colour, quickly becoming tarnished with a grey powder. An analysis of the compound gave percentages which corresponded exactly with the formula Na_2Sn , showing it to be of the type of stannous compounds represented by the oxide SnO . The action of this substance on water is interesting from a teacher's point of view; it being specifically heavier than water, quantities of hydrogen can be safely prepared for class demonstrations. An excess of sodium gave an alloy which decomposed water with such violence that the hydrogen evolved was ignited, the heat of combination being localised owing to the specific gravity of the alloy. To ensure that the temperature used in the preparation of the alloy was sufficient to volatilise the free sodium, a quantity of pure sodium was heated in a crucible with the necessary precautions for the exclusion of air, at the same temperature as that used in the preparation of the compound. As a result only a slight trace of oxide was obtained.

Science School, Penzance,
December 23, 1891.

A READY METHOD OF DISTINGUISHING BETWEEN ALPHA- AND BETA-NAPHTHOL.

By F. W. RICHARDSON, F.C.S., &c.

HAVING occasion to test the contents of two bottles to ascertain which was alpha- and which beta-naphthol, I applied the methods of N. Yvon, described in the *CHEMICAL NEWS* (vol. lxiv., p. 321), but obtained very unsatisfactory results; indeed process (2), as might be expected, gave no result whatever.

Remembering that the difference between the azo-dyes "Orange I." and "Orange II." is entirely due to the fact that while for the preparation of the former dye α -naphthol is used, β -naphthol is required for the latter, I worked out the following process:—

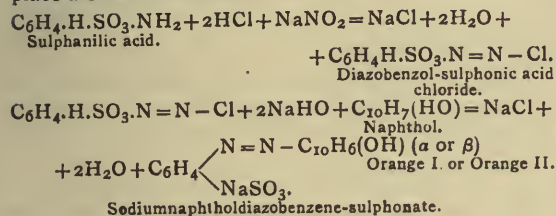
Dissolve about 5 c.grms. of sulphanilic acid in a little water containing about 5 c.c. of normal soda; add 5 c.c.

of normal sulphuric acid, and mix the solution with 2 c.grms. of sodium nitrite dissolved in a few drops of water.

Dissolve a little (about 4 c.grms.) of the naphthol by the aid of a few drops (0.5 c.c.) of normal soda, and into this solution pour the diazotised sulphanilic acid. With α -naphthol the liquid becomes dark blood-red; with β -naphthol only a reddish-yellow colour is produced; this difference is most marked when the dyes are salted out.

The α -naphthol dye becomes dark brown with dilute sulphuric acid, while the β -naphthol compound is quite unchanged: this last reaction is very distinctive.

The equations representing the changes which take place are as follows:—



A TABULAR EXPRESSION OF THE PERIODIC RELATIONS OF THE ELEMENTS.

By HENRY BASSETT.

(Concluded from p. 4).

THE third fold of the paper covers up Ta and W, and we get the following:—

TABLE III.

Li	Na	K	Rb	?	?
Be	Mg	Ca	Sr	?	?
B	Al	Sc	Y	Tb	?
C	Si	Ti	Zr	Ho	?
N	P	V	Nb	?	?
O	S	Cr	Mo	Er	?
F	Cl	Mn	?	?	?

Our knowledge of the general chemical characters of the rare earth-metals, now found to the right of the table, is far too slight at present to warrant many remarks, but Tb, which gives a strongly basic oxide, appropriately follows Y, and Er, Mo, and Cr have at least one well-marked similarity, that of forming strongly-coloured compounds, and I cannot but think it probable that further investigation may show other analogies in this part of the primary table also.

The last fold of the paper covers up Tb, Ho, and Er, and we finally obtain:—

TABLE IV.

Li	Na	K	Rb	Cs	?
Be	Mg	Ca	Sr	Ba	?
B	Al	Sc	Y	La	?
C	Si	Ti	Zr	Ce	Th
N	P	V	Nb	Ndy	?
O	S	Cr	Mo	Pdy	U
F	Cl	Mn	?	?	?

Now at last we see all the alkali metals in an unbroken series; then we have Be, Mg, and the alkaline earth metals all together, followed by a complete series of 3-valent elements showing very close analogies, and a regular gradation of properties from left to right. In the lower part of the table the resemblances are less pronounced, but we cannot overlook the conjunction of a still larger number of colorific elements than in Table III. The Tables I. and IV. are, in fact, complementary, the closest analogies and most complete gradation being

shown in the three bottom lines in the former, and in the three top lines in the latter.

It will be readily seen that this series of tables is actually derived from the first by successive upward shifts of the first and second pairs of groups or periods, and I have devised a sliding model for the illustration of the complete system, which appears to agree with facts as far as we know them, and to give a simple, clear, and suggestive expression of the relations of the first typical small periods with the succeeding large ones, and with the other small periods of which these are built up. Many points of interest will present themselves on examination of the primary table, but their discussion would unduly extend this paper, and would besides be premature.

By calling H the first period, the old distinguishing numbers of the others, so well known to students of Mendeleeff's table, would be retained; but surely the term must imply a group of elements? If any such existed between H and Li the resulting period would show very little numerical analogy with any of the others, and, from this and some other considerations, I am inclined to think that hydrogen might, without great impropriety, be called the Anteperiodic element. I will not pursue the subject, but it is one on which the ghost of Froust would certainly have a great deal to say.

One important point remains. While the atomic weights are the prime foundation of the system, the atomic volumes are also of great value from the direct indications which they give as to the simple or complex character of the periods. Starting from the highest member of a period, whether single or double, they gradually diminish to some intermediate or central point, and then increase to the lowest. The quadruple Cs period given in the primary table above should function as a whole from this point of view, like the two preceding double periods. I consider there are some indications that it will be found to do so, and to have its minimum in the Os interperiodic group, but for proof of this many essential data are at present wanting. There is very little doubt that metallic Ta has not been prepared, and the upper members are also unknown in the metallic state till we reach Di. We must therefore await determinations of the specific gravities of Ta, and of some few of the higher members, say Yb, Er, and Sm. The atomic volumes of Th and U, the only known members of the following series, seem to show that they belong to a double period, which I have indicated in the table.

At a meeting of the Franklin Institute, on Sept. 15th, 1891, Mr. Waldron Shapleigh exhibited a magnificent collection of salts of the rare earths, and called attention to the fact that many of them would be rare no longer, hundreds of tons of their ores existing in North Carolina, Brazil, and elsewhere (CHEM. NEWS, Nov. 6, 1891). We may, therefore, confidently anticipate that the missing data will be forthcoming in the near future from the researches of the many distinguished workers who have already done so much towards the elucidation of a subject which is perhaps one of the most interesting and important occupying the attention of the chemical world.

FUNDAMENTAL PRINCIPLES TO SERVE IN THE CHEMICAL EXAMINATION OF WINES, AND IN THE JUDGMENT TO BE PASSED UPON THEM.

By W. FRESSENIUS and B. HAAS.

A. Chemical Examination.

1. For the determination of the specific gravity a pycnometric examination at 15° C. is to serve as the basis; it must be given accurately to four decimal places.
2. The results must be given in grammes per 100 c.c., or per litre.
3. The alcohol is to be determined by the distillation method; the specific gravity of the weighed distillate is

taken with the pycnometer at 15° C. (respectively 15.5° and the proportion of alcohol calculated accordingly).

4. The proportion of extract :—(a). Of wines with an extract amounting to 3 grms. per 100 c.c., 50 c.c. are evaporated in a flat-bottomed platinum capsule upon the water-bath; the residue is heated for 2½ hours in water drying niche, and finally cooled in the exsiccator and weighed. (b). Wines containing a higher proportion of extract are to be diluted with water, so as not to contain more than 3 grms. extract in 100 c.c. The residue is to be treated as above. (c). For sweet wines an indirect method of determining the extract from the sp. gr. of the wine after removal of the alcohol is to be preferred.

5. The free acid is determined by titration with potassa- or soda-lye suitably diluted, using litmus-paper as indicator, and calculating the result as tartaric acid ($C_4H_6O_6$). Volatile acids are to be determined by distillation in watery vapour, and to be expressed as acetic acid ($C_2H_4O_2$).

6. The determination of the glycerin in ordinary wines (not sweet wines) is to be carried out according to the method agreed on by the German or Austrian chemists, without a correction for evaporation. The determination of glycerin in sweet wines does not give accurate results. If required, Borgmann's method is to be preferred.

7. Mineral matter is found by incinerating the residue from the evaporation of 50 c.c.

8. Polarisation may often be dispensed with in dry wines; in sweet wines it must be resorted to before and after inversion.

9. Sugar is to be determined according to Soxhlet or Allihn, and expressed as grape-sugar. If the proportion of sugar is considerable, or if the difference between the proportion of extract and the quantity of directly reducible sugar is exceptionally high, a determination of sugar must be carried out after inversion.

10. Sulphuric acid is precipitated directly with barium chloride in wine acidulated with hydrochloric acid, and determined in the ordinary manner.

11. Sulphurous acid is determined by distilling a portion of the wine to which phosphoric acid has been added, receiving the distillate in solution of iodine, and determining the sulphuric acid thus formed.

12. The determination of phosphoric acid is to be effected in the ash of the molybdc method.

13. Tartar is to be determined by Nessler and Barth's method.

14. A determination of free tartaric acid takes place only if required to complete the other analytical results. A mere qualitative detection is useless. For the qualitative determination of free tartaric acid along with that of tartar the method of B. Haas (*Zeit. Nahrungsmittel und Hygiene*, 1888, p. 100) is recommended.

15. Examination for Colouring-matters :—(a). Vegetable colours. The wine is mixed with an excess of lead acetate and filtered. The colour of the precipitate in a genuine red wine may be greyish-blue, bluish-grey, ash-colour, or greenish. If a precipitate is obtained not greatly differing from these colours, the search for other vegetable pigments can give no certain result. The colouring-matter of bilberries give a blue precipitate; mallow and elder berries a green. The colour of phyto-lacca berries differs from that of red wine by giving a red-violet precipitate with lead. (b). Tar colours. As the colouring of any article of food, &c., with tar colours is illegal, it is sufficient to prove the presence of any such colouring matter in wine. In most cases a tar colour may be recognised in wine by the following three methods :—

a. By shaking the filtrate from the basic lead acetate with amyl alcohol, and testing the coloured amyl alcohol. For this purpose we require 100 c.c. of wine and 30 c.c. of solution of basic lead acetate.

β. By the wool test according to Strohmmer and Arata (dyeing wool).

γ. By Cazeneuve's mercuric-oxide test (*Vierteljahr-schrift fur Chemie der Nahrungsmittel*, 1886, p. 80).

The following two tests are recommended in addition :—

δ. Shaking the wine with ether before and after supersaturation with ammonia.

ε. A similar shaking with amyl alcohol.

16. Salicylic acid is best sought for by shaking the wine up with carbon disulphide in a mixture of equal volumes of ether and petroleum ether, evaporating down and testing the residue with ferric chloride. If much more than 100 c.c. of wine are used, a faint colour may be occasioned by the normal constituents of wine.

17. For detecting saccharine C. Schmitt's method is recommended. The wine is shaken up with a mixture of equal parts of ether and petroleum ether, and the evaporated residue is melted with sodium hydroxide. Not more than 100 c.c. of wine must be used for this test.

18. Nitric acid is sought for by adding 1 to 3 drops of wine to a solution of diphenylamine in (pure) concentrated sulphuric acid.—*Zeitschrift fur Anal. Chemie*, xxx., Part 4.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 5).

HENCE it follows, as a matter of course, that so-called contact effects, like, e.g., the reaction between wood-charcoal which has absorbed chlorine and hydrogen conveyed in darkness is introduced by the high tensions and consequent condensations in the spaces of the charcoal which are in part capillary and in part very uneven, possessing a very large surface, in which spaces the reaction takes place.

The much disputed action of platinum black is without any doubt analogous. Gases—especially atmospheric air, watery vapour, &c.—are condensed upon the extremely porous or finely divided platinum, and the atmospheric oxygen becomes thus extremely capable of reaction, and is transformed into an active so-called allotropic state.

It is common to all these reactions and conversions that capillary spaces occur in very porous third bodies in which the substances capable of reaction undergo great condensation.

In all such cases there is given the possibility, even the probability,—we might in some instances say the necessity,—of an intense chemical action which must be proportional to the magnitude of the tension.

In capillary spaces there can take place from a certain size onward merely an ordinary chemical process, since below a certain size, capable of being experimentally determined, no action of mass is possible. Action of mass is possible only where masses are possible, therefore with a certain number of mols. Such truly capillary spaces where the mols. cannot accumulate up to the number necessary for effecting an ordinary chemical reaction exclude an action of masses, a chemical equilibrium, and they are the field for true condensations, for the most intense chemical transformations, for spontaneous decomposition. Here there occur, in place of the coarse reaction of masses, the most subtle individual reactions, as we may call them. Here there do not meet large armies of mols. with the corresponding partial pressures; there occurs here, the rather, an active and continual single combat, a splitting up of the mols. as they come in the scope of the atoms engaged in violent competition for their affinities. No equalisation of the entire atomic energy present, no maximum of entropy, is possible. On the contrary, other internal relations, e.g., between the height reached, consequently the ascending force and the molecular weights come into their rights. A number of true chemical compounds fall as dead material out of the

incessant chemism going on connected with the first five accompanying phenomena already enumerated, whilst of the accessory material only a strictly defined portion conditioned by affinity arrives at scission and synthesis.

But this individual chemical reaction is totally distinct from the chemical mass reaction in the test-tube, in the retort, in the flask. An entire series of physical conditions are here of the greatest influence, which are there unimportant, *e.g.*, the presence or absence of light, the fluctuation of temperature for the fraction of a degree, the greater or less elasticity of the sides of the containing vessels, agitation, and other conditions which are compensated in mass reaction, but not in individual reaction.

The entire consideration thus laid down can be completely applied to the chemism of living protoplasm. Here there certainly occurs not exclusively a chemical mass reaction, but principally a chemical reaction individualised in the highest degree, since the microscopic minuteness of the spaces does not permit of mass reaction.

The system of unenclosed capillaries of the network in protoplasm (the latter matter having been first made known by Karl Frommann in a series of admirable investigations), the intervals and the minutest vacuola, with their fissures often remarkably permanent and often as remarkably mutable, are to be regarded as the true seat of chemical transformation in protoplasm, and hence in the organism altogether. Even when non-capillary tubes are recognised in such protoplasm as bands with a double outline—the universal occurrence of such must be excluded—it is inconceivable that sideless channels and fissures, exceeding in fineness all ordinary capillaries, should not be present in every protoplasm in which a reticulated structure can be detected. That no protoplasm can exist without such a structure is almost universally admitted. That in presence of the nuclear division figures recognised by numerous observers with the most satisfactory agreement, in view of the mutations of the finer structure of protoplasms observed in embryonal as in developed, in animal as in vegetal, in normal as in pathological, tissues, the existence of the finest capillaries of vacuola or capillary fissures in the highest degree cannot be contested. For the different nature of the solid and liquid parts of the nucleus, of the nuclear membrane, the hyaline border, and even the cell-membrane itself, exclude the possibility of homogeneity existing, notwithstanding the constant presence of a reticular structure within any given protoplasmic tissue.

(To be continued.)

NITROHYDRIC ACID.

By TH. CURTIUS.

(Concluded from p. 5.)

NITROGEN AMMONIUM is precipitated from its alcoholic solution by ether as a snow-white powder, consisting of minute, anisotropic needles. If this powder is boiled for some time in absolute alcohol in a reflux-condenser it is entirely dissolved. On cooling, the substance separates out in large, massive, colourless leaflets, composed of individual crystals arranged in the form of stairs or of a fan. In this state the substance has a deceptive resemblance to ammonium chloride. It does not, however, crystallise in the regular system. From water, on evaporation *in vacuo*, we may obtain it in the form of large crystals, limpid as water, which become dull on exposure to the air. Nitrogen ammonium reacts faintly alkaline; it is not hygroscopic, dissolves readily in water and in alcohol at 80 per cent. It is sparingly soluble in absolute alcohol and insoluble in ether or benzene. It is distinguished by its extreme volatility, whether along with the vapours of alcohol or water or if preserved alone. If exposed to the air it disappears entirely by degrees, but

without any change. If gently heated a little above 100°, it may be sublimed from one place to another exactly like ammonium chloride, and is thus obtained in small glittering prisms. If rapidly heated in an open test-tube, it explodes with extreme violence.

Nitrogen Diammonium, N_5H_5 (Diammoniummonoazide).

Diamide ought to unite with one or with two mols. of nitrohydric acid to form the salts N_5H_5 and N_8H_6 . Hitherto I have only succeeded in obtaining N_5H_5 . It is prepared by superstratifying nitrogen ammonium with one mol. of hydrazine hydrate, and evaporating in the exsiccator in a shallow capsule. Further, very concentrated aqueous nitrohydric acid (obtained by distilling 60 grms. nitrogen lead with dilute sulphuric acid and watery vapour) mixed with hydrazine hydrate until litmus was turned distinctly blue, when the solution was left to spontaneous evaporation over potassa or sulphuric acid. Here also N_5H_5 crystallised out in place of N_8H_6 as it was expected, whilst nitrohydrogen was in part volatilised and absorbed by the caustic potassa under the bell. For analysis the substance was re-crystallised from alcohol.

On combustion in a current of oxygen, the salt exploded every time with extreme violence. But the nitrogen also could not be determined volumetrically by combustion along with copper oxide in a current of carbon dioxide, as on displacement of the air a large part of the substance was always volatilised. The compound was therefore dissolved in water, and its proportion of nitrohydric acid was precipitated as nitrogen silver by silver nitrate after the addition of a few drops of nitric acid. The substance, which is extremely hygroscopic, is effected in closed tubes. The precipitated nitrogen metal was first dried by section upon a weighed, perforated, porcelain capsule, and its desiccation was cautiously completed at 100°.

0.4949 grm. of the substance, dried over potassa lye and sulphuric acid, yielded, on precipitation with silver nitrate, 0.9727 AgN_3 , corresponding to 0.2818 grm. nitrohydrogen.

	Calculated for $N_5H_5.N_2H_4$.	Found.
N_3H_4 43	57.35	56.95

An attempt was made to shake out the base combined with the acid in the nitric filtrate from nitrogen silver by the cautious addition of benzaldehyde. As soon as an excess of this solvent was added a portion of the benzaldehyde formed re-dissolved in the liquid containing benzaldehyde, so that the quantity of diamide found was smaller than that which the ascertained acidity of the salt required.

Nitrogen diammonium (diammoniummonoazide), N_5H_5 , crystallises in stout anisotropic prisms, an inch in length and of a vitreous lustre; they melt at about 50°, deliquesce in a short time in the air, and gradually evaporate at common temperatures, but more rapidly along with the vapours of alcohol or water. They are sparingly soluble in boiling alcohol, from which they crystallise in shining leaves. The crystals burn quietly with a smoky flame, of a slightly yellow colour if kindled with a flame without leaving traces of soot or residue. Metallic surfaces upon which this combustion takes place are freed from every trace of oxide by the reductive action of the ignited hydrogen evolved, and appear as if polished.

On rapid heating in the air, as on contact with a wire heated to whiteness, or on ignition by means of detonating nitrogen metals or fulminates, there occurs a fearful explosion. Even in the moist deliquescent condition, these explosive properties are retained.—*Berichte der Deutschen Chemischen Gesellschaft*, vol. xxiv., pp. 33-41.

Determination of Lignine in Woods.—R. Benedikt and M. Bamberger.—(*Monatshfte für Chemie*).—As Benedikt and Grüssner employ the so-called methyl number for the recognition of oils, fats, and waxes, the authors aim at discovering the percentage of lignine in a wood by means of its methyl number. They give a tabular conspectus of their results.

THE DETECTION AND DETERMINATION OF POTASSIUM SPECTROSCOPICALLY.*

By F. A. GOOCH and T. S. HART.

BUNSEN and Kirchhoff originally determined the delicacy of the spectroscopic test for potassium by exploding in a darkened room a mixture of potassium chlorate with milk sugar, and observing the amount of finely divided chloride which it was necessary to diffuse through the given space in order to bring out unmistakably the spectrum of the metal. These investigators were able to state that the presence of no more than 1-1000 of a m.grm. of the potassium salt is sufficient to give to the flame the characteristic spectrum of the element. By similar methods the delicacy of the tests for lithium carbonate and sodium chlorate were shown to be a thousand times and three thousand times as delicate respectively. Practically, the detection of lithium and sodium spectroscopically is extremely easy and satisfactory, the only difficulty being that the exceeding delicacy of the sodium test, and the ubiquitousness of sodium salts often make a decision doubtful as to whether that element is present essentially in the substance under examination or by accident. With potassium the case is different, and experience shows that when the test is to be made for very small amounts of potassium, the simple method in vogue for developing the luminosity of lithium and sodium—the dipping of a single loop of platinum wire in the liquid or solid substance, and the placing of the loop in the Bunsen flame—fails, because, as it seems to us, so great a proportion of the material is dispersed before the heat of the flame effects the dissociation of the metal which precedes the production of the spectrum.

We have endeavoured to improve the conditions of exposure of the test substance by making use of more powerful flames and by substituting for the single loop the hollow coils of platinum wire first recommended, so far as has come to our knowledge, by Truchot (*Comp. Rend.*, lxxviii., 1022) in the description of a method for the quantitative determination of lithium. Such coils are easily made by winding the wire somewhat obliquely about a rod of suitable size, pressing the coils close together, and gathering the free ends into a twisted handle. The size of the coils is adjustable without difficulty, so that each coil may be made to hold almost exactly any appropriate amount, and to take up this amount with very little variation in successive fillings, provided only that the precaution be taken in the process of filling to plunge the coil while hot into the liquid, and to keep its axis inclined obliquely to the surface of the liquid while withdrawing it. How closely the capacity of such coils may be adjusted, and how uniformly they may be filled, is shown in the figures of the accompanying record.

Weight of—	I. Grm.	II. Grm.	III. Grm.	IV. Grm.	V. Grm.	VI. Grm.
Filled coil—						
0.1996	0.2780	0.2794	0.2844	0.3572	0.3296	
0.1996	0.2780	0.2794	0.2845	0.3571	0.3296	
0.1996	0.2780	0.2794	0.2844	0.3572	0.3298	
0.1996	0.2780	0.2794	0.2845	0.3571	0.3298	
0.1996	0.2781	0.2794	0.2844	0.3571	0.3296	
Empty coil—						
0.1986	0.2760	0.2764	0.2804	0.3521	0.3100	
Contents (mean)—						
0.0010	0.00202	0.0030	0.00404	0.00504	0.01968	

It is plain that we have in these coils simple means of taking up known amounts of material in solution; and by gentle heating, the liquid may be evaporated and the solid material left thinly and uniformly spread, not easily

detachable, and so in condition to be acted upon with effect when brought to the flame. The evaporation may be conducted with little danger of loss of material by holding the handle of the coil across the flame with the coil proper at a safe distance outside; but we have generally, and preferably, used a hot radiator, over which the coils are exposed, the handles resting upon a flat asbestos ring. The burner which we have used in heating the coils before the spectroscope is of the Muencke pattern, and gives a powerful flame 3 c.m. wide at its base. We have generally adjusted the flame to a height of 20 c.m., and have introduced the coil, after thorough drying, just within the outer mantle, on the side next the spectroscope, with the axis transverse to the slit of the spectroscope and the handle across the body of the flame. In cleaning the coils we have found it convenient to heat them in the flame of an Argand burner of the Fletcher pattern, beneath which is burned in a small lamp alcohol containing about a twentieth of its volume of chloroform. The products of combustion of the alcohol and chloroform are conveyed to the interior of the flame above by a glass funnel fitted by a cork to the tube of the Argand burner. This arrangement of apparatus gives a hot colourless flame through which hydrochloric acid is constantly diffused in condition to clean the wires completely and without attention. The spectroscope which we have employed is a well made single prism instrument provided with a scale and a movable observing telescope, so that different portions of the spectrum may be viewed or cut off at will. The slit is adjustable, but for measuring its width we have been obliged to have recourse to the device of closing it upon wires of known gauge. Our work has been done in the ordinary diffused light of the laboratory, care having been taken to cut off from the room direct sunlight only; but in observing it has been our custom to shield the eye in use as completely as possible with the hand or with a dark handkerchief, and to cover the eye not in use. We have found it desirable to use the scale of the instrument, illuminated to the lowest degree of visibility, to aid the eye in placing barely visible lines.

Upon experimenting with the apparatus described, it was found that the largest coil used was best adapted to our purpose, and, accordingly, in all the experiments made subsequently and recorded in the following account, coils holding 1.50 of a grm. of water, measuring 2 m.m. in diameter by 1 c.m. in length, made of No. 28 wire (0.32 m.m. in diameter), and wound in about thirty turns, were the ones employed. With these coils and the flame adjusted to a height of 20 c.m. we have been able to recognise the presence of potassium, taken in the form of the chloride, in a coil-full of liquid containing 0.00066 grm. of the metal in 10 c.m.³, when the slit had a width of 0.18 m.m., and containing 0.0005 grm. in the same volume of solution, when the slit was set 0.23 m.m. wide. That is to say, 1.750 m.grm. of potassium to the coil-full produces a line distinctly visible with a slit of 0.18 m.m., and 1.000 m.grm. with a slit of 0.23 m.m., and it is evident that this practical method of producing the spectrum of potassium gives results of a delicacy approaching that indicated in the experiments of Bunsen and Kirchhoff.

These determinations were made with pure potassium chloride carefully prepared from the chlorate, but in practical analysis it almost always happens that sodium is also present. Experiments were therefore made to determine the influence of varying amounts of the latter upon the visibility of the potassium line. The dilution of the potassium chloride was adjusted nearly to the last limit of visibility, so that a coil-full of the liquid should contain 1.700 m.grm., or 1.000 m.grm. of the element, according as the slit was 0.18 m.m. or 0.23 m.m. wide; to this solution were added weighed amounts of pure sodium chloride twice re-precipitated and washed by hydrochloric acid, and the spectroscopic tests were carried out as before, the sodium line being kept within the field of view with the potassium line.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlii., December, 1891.

Weight of K in a coil-full. M.grm.	Weight of Na in a coil-full. M.grm.	Ratio of Na : K.	Width of slit. M.m.	Number of trials.	Characteristic of line.
0.0010	0.0000	0 : 1	0.23	3	visible
0.0010	0.0020	2 : 1	0.23	3	"
0.0010	0.0100	10 : 1	0.23	3	"
0.0010	0.0200	20 : 1	0.23	3	"
0.0010	0.0400	40 : 1	0.23	3	"
0.0010	0.0500	50 : 1	0.23	4	{ very faint or none
0.0010	0.1000	100 : 1	0.23	3	none
0.0010	0.2000	200 : 1	0.23	3	"
0.0014	0.0000	0 : 1	0.18	3	visible
0.0014	0.0560	40 : 1	0.18	3	"
0.0014	0.0700	50 : 1	0.18	3	"
0.0014	0.1400	100 : 1	0.18	2	"
0.0014	0.1400	100 : 1	0.18	2	none

It is obvious from these results that a considerable amount of sodium may be present in the flame when the sodium line is in full view in the spectrum, and the slit adjusted to nearly the lowest limit of visibility of pure potassium, without interfering with the appearance of the potassium line, but that a quantity of sodium amounting to a hundred times that of the potassium is sufficient to entirely overpower the spectrum of the potassium. The inference is plain that the proportion of sodium to potassium should not be permitted to reach 100 : 1 when it is desirable to bring out the full delicacy of the spectroscopic test with the sodium line in the field of view. When too great a proportion of sodium is present, its influence may be moderated by throwing the sodium line out of view, if the instrument in use possesses the necessary adjustment; otherwise, it is easy to effect a partial separation of the sodium chloride from the potassium chloride, before bringing the solution to the test, by precipitating with alcohol. Our experience shows that the delicacy of the test for potassium is not impaired materially by such treatment of the mixed chlorides. We found, for example, that 0.0070 grm. of potassium chloride mixed with 0.5 grm. of pure sodium chloride, dissolved in the least amount of water, and extracted carefully by about 7 c.m.³ of absolute alcohol applied in successive portions, was so completely retained in solution and separated from sodium, that a coil-full taken from the solution diluted to 140 c.m.³ gave the spectroscopic test for potassium distinctly with the slit at 0.23 m.m. In this case, at least, the treatment did not diminish the delicacy of the test; for, a coil-full of the diluted solution could not have contained more than 1-1000th m.grm. of potassium, if nothing had been lost. It was found, in like manner, that, by taking pains to evaporate the alcoholic extract, and to dissolve the residue in a drop of water, 0.0001 grm. of potassium originally present as the chloride with 0.5 grm. of sodium chloride, was easily found. By turning the observing telescope so as to cut off as completely as possible the sodium light, we were able to detect potassium in four successive tests of a drop of the final solution which was just large enough to fill the coil four times, when the original amount of potassium present with 0.5 grm. of sodium chloride was 0.00001 grm. This is equivalent to detecting 1-400th m.grm. of potassium in a drop large enough to fill the coil once. We were assured of the entire absence of potassium from the sodium chloride which we used by the fact that the similar extraction of 1 grm. of the salt by alcohol left a residue which yielded no line of potassium when examined spectroscopically. It is, perhaps, worth noting, in passing, that the coil may be made to pick up a drop of a size only sufficient to fill it by simply touching the coil while hissing hot to the drop.

Certain experiments in which the method of manipulation which we have described was applied to the determination of potassium salts other than the chloride indicated that the test is less delicate in the case of the sulphate, and rather more delicate in the case of the

carbonate. We were able to find the red line of potassium unmistakably, when only 1-2000th of a milligram. of potassium was introduced into the flame in the form of the carbonate.

The quantitative determination of potassium by the spectroscope has never, so far as we know, been accomplished heretofore. Sodium appears to have been successfully estimated by Champion, Pellet, and Grenier (*Compt. Rend.*, lxxvi., 707) by the use of comparison flames, produced by the aid of complex mechanism, and a spectrophotometer of original construction. Lithium has been determined more simply, Truchot (*Compt. Rend.*, lxxviii., 1022) having been the first to suggest a method of manipulation which was modified by Ballmann (*Zeitschr. für Anal. Chem.*, xiv., 297) and taken up later by Bell (*Am. Chem. Jour.*, vii., 35) apparently without knowledge of the previous work on the same line. Truchot's method consists in comparing the duration and strength of the spectral lines developed by exposure to the Bunsen flame of portions taken up in a platinum loop from the test-solution and standard solutions of different strength. No analytical proofs of the value of the method were given, and accuracy was not claimed beyond the recognition of differences of from three to four milligrams. in a litre of liquid when amounts not exceeding forty milligrams. per litre were compared. Ballmann discards as valueless the observation of the duration of the spectral line, advocates the dilution of the test and standard solutions to the absolute extinction of the line, and employs hollow cones, measuring 2.5 m.m. by 3.5 m.m., to carry the liquids to the flame. Bell follows Ballmann's method of diluting the solutions to be compared to a common condition, but takes the vanishing point of the line instead of the point of absolute invisibility, and makes his loops of platinum very small. Both Ballmann and Bell were able to estimate thallium similarly, but neither determined potassium, Bell declaring specifically that the method is inapplicable to the handling of that element.

Our success in determining potassium qualitatively by the use of powerful flames and coils of large dimensions was such as to encourage the attempt to apply quantitatively the same method of manipulating; and from certain preliminary experiments looking in this direction we found it best, for our purpose at least, to fall back upon Truchot's method of comparing visible lines, rather than to try to fix the vanishing point or the point of extinction of the spectral line. We chose a dilution of the standard solution which corresponds to the presence of 1-500th m.g. of potassium to the coil-full, and set the slit at a width of 0.23 m.m., having found it most advantageous to work with lines for comparison bright enough to be visible without much effort. Our mode of proceeding is to dilute the test-solution until the line given by the potassium contained in a coil-full is of the same brightness as that given by the same quantity of the standard solution. From the final volume of the test solution the quantity of potassium present in it is directly calculable; for, since any given volume of the test-solution at its final dilution contains exactly the same amount of potassium as the same volume of the standard solution, we have only to multiply the number expressing the volume in cubic centimetres of the test-solution by the weight in grammes of the potassium contained in one cubic centimetre of the standard in order to obtain the weight in grammes of potassium in the whole test-solution. We found it convenient to use several coils adjusted to the same capacity, and to clean, fill, dry, and ignite them before the spectroscope in the manner previously described. From time to time the capacity of the coils should be readjusted, or else the final comparison tests should be made with a single coil. It is essential that the eye of the observer should be kept as nearly as possible in the same condition of sensitiveness and in the same position in making the comparisons, and to accomplish this end we found it best to hold the eye at the observing telescope during the entire interval between the exposures, to shade it care-

fully by the hand, or otherwise, to cover the eye not in use, to cut off all direct sun-light from the work-table (though the diffused light of the room is not objectionable), and to light the comparison scale of the spectroscope to the faintest possible visibility in order to fix exactly the position in which the line is to be sought. It is important, too, that the trials of the test and standard should come as closely together as possible in point of time. The observations of a series should be made by the same individual, the preparation and exposure of the wires being made by another. It is not possible to attain the best results in such work single-handed. The dilution of the test-solution is made conveniently, and with sufficient accuracy, in 100 c.m.³ cylinders graduated to half cubic centimetres, the mixture being made thorough by passing the solution from vessel to vessel. It is often advantageous to divide a liquid which is to be diluted, and to work with aliquot portions, so that it may be possible to retrace a step without trouble in case a portion of the solution has been unwittingly diluted too much; such a mode of proceeding is, of course, necessary when the final dilution must exceed 100 c.m.³, unless large graduates are called into use. Excepting the cases of very concentrated solutions, no significant loss of material is occasioned by the filling of the coils, the error thus introduced being trivial in comparison with that inherent in all photometric processes. The following is the record of our experience in the comparison of solutions of pure potassium chloride, the strength of the test solution being unknown to the observer.

EXPERIMENT I.		EXPERIMENT II.	
Volume of test-solution.	Characteristic of line compared with standard.	Volume of test-solution.	Characteristic of line compared with standard.
20 c.m. ³	stronger	30 c.m. ³	stronger
50 "	stronger	60 "	stronger
100 "	stronger	82 "	weaker
110 "	stronger	70 "	stronger
120 "	stronger	76 "	stronger
150 "	like	78 "	stronger
200 "	weaker	80 "	like
160 "	weaker		
150 "	like		
(150 × 0.0001 = 0.0150)		(80 × 0.0001 = 0.0080)	
Potassium found	0.0150 grm.	Potassium found	0.0080
" taken	0.0150 "	" taken	0.0080
Limits on either side	{ 0.0120 "	Limits on either side	{ 0.0078
	{ 0.0160 "		{ 0.0082
Error.. ..	0.0000 "	Error	0.0000

These results show a degree of accuracy in the process quite unexpected. In the former no attempt was made to approximate as closely as possible to the limits of dilution on both sides of the condition of equal brightness in test and standard, but in the latter great care was taken in this respect, and the possible error cannot exceed two and a half per cent of the entire amount of potassium involved.

(To be continued).

CORRESPONDENCE.

DANGERS OF WEED-KILLERS."

To the Editor of the Chemical News.

SIR,—My attention has been called to a paragraph in the CHEMICAL NEWS (vol. lxiv., p. 265) commenting on the dangerous practice of selling to ignorant workmen casks of arsenical preparations as "weed-killers."

I can fully confirm the statement made as to the prevalence of this procedure. Some time since I was

consulted by a client, who made such weed-killers, as to the easiest mode of obtaining an arsenical preparation in a convenient form. Of course I gave him the chemical advice required, but at the same time I felt bound to remonstrate with him on the danger accruing from such practice; and I am happy to say that, consequent on my protest, he abandoned the use of arsenic.

As a matter of fact I suggested that he should first of all take legal advice as to his qualification for selling arsenic as simply "weed-killer," and, as I had fully anticipated, the reply was adverse to him. Under these circumstances it would seem very desirable that any manufacturers who may be still selling arsenic, without any adequate caution, as "weed-killer," should be brought to book. I will only add that the arsenic is in the very soluble—and therefore especially dangerous—form of arsenite of soda.—I am, &c.,

F. H. PERRY COSTE.

Analytical Laboratory, 7, Fowkes Buildings,
Great Tower St., E.C., Dec. 29, 1891.

THE NEW METHYLATED SPIRIT.

To the Editor of the Chemical News.

SIR,—May I offer a suggestion with regard to this matter? We may assume that the Revenue authorities have no object in view save the prevention of drinking alcohol which has been allowed to pass duty free, for it can hardly be possible that they are taking this action, so plainly against the interest of very many people, merely with a view of increasing the Revenue.

Ought they not, therefore, to be ready to allow the spirit to be sold to all persons who are ready to enter their names (accompanied if necessary by references) in a book kept by the tradesman supplying the spirit, which book could be inspected by the Revenue officer?

Or, if this course is not sufficiently stringent, might not a license at a small sum (say 3s. or 4s. per annum) be issued to persons applying for the authority to purchase and use the spirit for stated purposes?

Unless some such modification is allowed by the Revenue their action must tend to check research of many kinds, and injure the position of industrial chemists.

—I am, &c.,

C. G. MOOR.

Vicarage, St. Clement, near Truro,
Jan. 2, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxliii., No. 25, December 21, 1891.

This issue gives an account of the annual public session of the Academy held on December 21, 1891, for the purpose of awarding the numerous prizes at its disposal for scientific researches.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 8, October 20, 1891.

This issue contains merely abstracts from other journals.

Series 3, Vol. vi., No. 9.

Researches on the Colouring-Matters derived from Triphenylmethane.—E. Noelting.—This seventh paper gives a description of the derivatives of triphenyl-

THE CHEMICAL NEWS.

Vol. LXV., No. 1676.

A RAPID METHOD OF DETERMINING THE COMPOSITION OF LUBRICATING OILS.

By HAROLD GRIPPER, F.C.S.

THE great majority of the oils now used for machine-lubricating are mixtures of hydrocarbon and saponifiable oils. The existing methods for the determination of these constituents are accurate and easily worked, but somewhat tedious, all consisting in saponification and subsequent separation by extraction of the hydrocarbons with ether. The usual process (described in Allen's "Commercial Organic Analysis," vol. ii., p. 83) involves saponification, evaporation of the alcohol, dilution with water and cooling, separation in a separating funnel with ether, and finally evaporation of the ethereal layer and weighing of the residue. All this takes time, even if the separation in the separating funnel takes place rapidly, which is not always the case.

The following process I have found useful when a number of samples have to be examined at the same time, and when results approximately correct only are required, as is often the case in this laboratory. The results obtained are within 2 or 3 per cent of the truth. The method is simply an extension of the well-known Koettstorfer process. 2½ grms. of the sample are saponified in the usual way with 25 c.c. of a solution of alcoholic potash about N/3 (with oils containing more than 50 per cent of saponifiable oil the usual N/2 strength may be used). When saponification is complete the titration is made in the ordinary way with N/2 HCl, using phenolphthalein as indicator, and a blank experiment having been made to estimate the strength of the alcoholic potash used, the percentage of KHO used by the sample is calculated.

The saponifiable oils chiefly used in the making of mixtures for lubricating purposes are—

	KHO absorp- tion.	Saponification equivalent.
Brown cotton-seed ..	22·27 per cent.	252
„ rape	20·03 „	280
Neatsfoot	18·70 „	300
Lard	19·30 „	290
Tallow	17·90 „	313
Castor		

The potash absorptions therefore vary between 17·90 per cent and 22·27 per cent. It is necessary to take the mean of these figures (20·08 per cent) as the potash absorption of the unknown mixture of saponifiable matter in a lubricating oil. Then $100·0/20·08 = 4·98$ parts of the oil are saponifiable by 1 part of KHO. Therefore if the percentage of KHO absorbed by the sample be multiplied by 4·98, the amount of saponifiable matter present will be obtained. Or the calculation may be simplified by multiplying the number of c.c. of N/2 HCl (corresponding to KHO neutralised) by $(0·02805 \times 40 \times 4·98) = 5·587$. The proportion of saponifiable oils is thus obtained. The amount of hydrocarbon oil is ascertained by difference.

But it is necessary to know the specific gravity of the hydrocarbon oils. In order to estimate this, the liquid in the oil flask is, immediately after titration, raised again to the boiling-point, and poured through a filter paper which has been saturated with boiling water. The alcoholic solution of soap and KCl will run through in two or three minutes, the hydrocarbon oils remaining on the filter. They are washed once with boiling water, and the specific gravity may then be taken by Hager's method. It is not necessary to wash the oil more than once, since in making Hager's test the globule of oil dropped into the alcoholic liquid is immediately cleansed thereby from all impurities. The specific gravity of the hydrocarbon oils and of the original mixture being known, the specific gravity of the saponifiable oils may be calculated by difference.

By this method an analysis may be completed, including the calculation of results, within an hour of the commencement of the saponification, and in examining a series it is of great advantage, a dozen samples being easily completed in a day. The only source of error is in the fact that the nature of the saponifiable oil, and therefore its exact saponification equivalent, is unknown.

By titration.

- | | |
|--|---|
| I. 78·3 per cent of hydrocarbon oil, sp. gr. 0·891 | } |
| 21·7 „ saponifiable oil, „ 0·950 | |
| 79·4 per cent of hydrocarbon oil, sp. gr. 0·891 | |
| 20·6 „ saponifiable oil, „ 0·955 | |
| 78·3 per cent of hydrocarbon oil, sp. gr. 0·891 | } |
| 21·7 „ saponifiable oil, „ 0·950 | |
| | |
| II. 72·7 per cent of hydrocarbon oil, sp. gr. 0·900 | } |
| 27·3 „ saponifiable oil, „ 0·973 | |
| | |
| III. 76·6 per cent of hydrocarbon oil, sp. gr. 0·882 | } |
| 23·4 „ saponifiable oil, „ 0·956 | |
| | |
| IV. 65·4 per cent of hydrocarbon oil, sp. gr. 0·887 | } |
| 34·6 „ saponifiable oil, „ 0·966 | |
| | |
| V. 79·9 per cent of hydrocarbon oil, sp. gr. 0·885 | } |
| 20·1 „ saponifiable oil, „ 0·963 | |
| 79·6 per cent of hydrocarbon oil, sp. gr. 0·885 | |
| 20·4 „ saponifiable oil, „ 0·962 | |
| 79·9 per cent of hydrocarbon oil, sp. gr. 0·885 | } |
| 20·1 „ saponifiable oil, „ 0·963 | |
| | |
| VI. 56·5 per cent of hydrocarbon oil, sp. gr. 0·906 | } |
| 43·5 „ saponifiable oil, „ 0·966 | |

By separation and weighing.

- | | |
|---|---|
| 79·3 per cent of hydrocarbon oil, sp. gr. 0·890 | } |
| 20·7 „ saponifiable oil, „ 0·957 | |
| | |
| 74·4 per cent of hydrocarbon oil, sp. gr. 0·900 | } |
| 25·6 „ saponifiable oil, „ 0·979 | |
| | |
| 76·7 per cent of hydrocarbon oil, sp. gr. 0·883 | } |
| 23·3 „ saponifiable oil, „ 0·953 | |
| | |
| 64·1 per cent of hydrocarbon oil, sp. gr. 0·886 | } |
| 35·9 „ saponifiable oil, „ 0·964 | |
| | |
| 79·8 per cent of hydrocarbon oil, sp. gr. 0·886 | } |
| 20·2 „ saponifiable oil, „ 0·959 | |
| | |
| 58·1 per cent of hydrocarbon oil, sp. gr. 0·908 | } |
| 41·9 „ saponifiable oil, „ 0·965 | |

The accompanying results were obtained by the process described, and by the usually accepted method of separation with ether and weighing the hydrocarbons. The results are in all cases in approximate and in some cases in close agreement.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 21.)

As on the large scale, e.g., in the liver biliary capillary ducts, without walls run among the cells we must here conceive that on the small scale, in the cells themselves, there are capillaries, devoid of walls, which are connected with each other and mediate the exchange of the assimilable matters with the soluble constituents of the cellular body. The cellular membrane, and in its default the mutable surface of the protoplasm, necessarily modified by contact with the surrounding medium, exerts a purely physical elective influence upon the matters which enter or which come forth. If it were otherwise, all ova which are developed in water must perish, and the known laws of osmosis would be inapplicable, for which we have no evidence. It is rather probable that in every protoplasmic tissue a certain class of substances is drawn in through the most superficial layer or skin in order thus to arrive in the protoplasmic capillaries, and ultimately to occasion distension, turgor, &c., whilst a certain number of substances which have been chemically modified in the internal spaces are prevented from escaping, so that growth and multiplication by the division of the superfluous nutriment is the necessary result; since the increase of mass occasioned by such intussusception, imbibition, and assimilation above a certain limit must cease; the condition for the individual processes, smallness of the entire space, and hence the absence of the action of mass.

The researches of W. Pfeffer on the membranes of the plasma, the vacuoles, the aggregate condition of the plasma, and on the osmotic processes in it, as well as a number of details observed by the best microscopists, supply our view with powerful supports.

But the necessity of capillary spaces in the protoplasm itself, for the occurrence of its entire chemism, has hitherto not been brought into prominence. These spaces are the seat of the fundamental chemical vital processes, the formation of carbon dioxide, of albumen, and of the consumption of oxygen. The currents which exist in every protoplasm as long as it lives, must be occasioned chiefly by the differences of pressure in the individual reactions. The osmotic pressure in the plasma may reach several atmospheres, whilst the counter pressure scarcely exceeds one.

It is therefore, at least, a highly probable hypothesis if we assume as the necessary foundation for all protoplasmic chemical activity, and, consequently for all vital processes, the constant presence of capillary spaces in every protoplasm, as in them the action of masses cannot be reached, and the single actions must accumulate.

Important as the cellular nucleus demonstrably is in many cases for metabolism, the idea of its being indispensable for the course of the processes of metabolism is refuted by the accumulated observations made on non-nucleated parts. In particular, the process of growth can no longer be referred to a function of the activity of the nucleus or of the cellular membrane. On the other hand, both are without question of the greatest influence in the maintenance of a certain kind of chemism in the capillary spaces. Even in the simplest osmotic pressures through a single thin membrane, the nature of such membrane, the temperature, the concentration of the solutions, and an entire series of physical conditions, have a determining action upon the final result. If then, nucleus and membrane have derived certain permanent properties by the

combination of adaptation and inheritance, we can well conceive that they both signify more as regulators for the progress of the assimilation and dissimilation of the protoplasm than as regulators; when both are wanting, metabolism and differentiation are not regulated. But the more one or the other part has become morphologically individualised by being accustomed always to the same external conditions, the same saline solutions, temperatures, degrees of pressure, &c., the more such a tissue loses its plasticity, and then in its internal spaces the individual chemical reactions must ensue, more and more in a certain direction rather than in any other, so that the capacity for adaptation becomes smaller and smaller and is finally lost. In its place comes the specific energy. But in every organism there remains so much protoplasm not specifically differentiated, which remains fit for every function in the leucocytes, and in the sexual secretions, that the protoplasm, even here, may be regarded as a kind of microcosm, in as far as it produces an immeasurable variety of forms, and thus maintains in action the incomprehensibly differentiated life on the surface of the earth.

(To be continued.)

SEPARATION OF BISMUTH AND LEAD.

By W. REMMLER.

THE volatility of bismuth chloride as contrasted with lead chloride has previously been utilised for the separation of the two metals. Rose and Fresenius report on this separation, Vogel (*Zeit. f. Analyt. Chemie*, xiii., 61) considers the most suitable temperature for the separation to be 360° to 370°. He remarks that the mixture must not be heated too strongly, as otherwise lead chloride may be driven off; whilst if the temperature is too low, bismuth chloride may be left behind. As it is difficult to hit the right temperature, the author, at the instigation of Prof. V. Meyer, attempted the separation by heating in the vapour of boiling sulphur, and has found that this method allows an easy and accurate separation. As a first experiment, he heated lead chloride in the sulphur bath to ascertain if it sublimed at the temperature of boiling sulphur, since Vogel states that lead chloride is volatilised at 400°. He constructed an apparatus which he used for the following separations:—In a test-tube, 20 c.m. in length, and 3—4 c.m. in diameter, there are placed about 20 grms. of sulphur. Into this tube there projects downwards a second narrower tube, about 16 c.m. in length, fixed above in a cork, which at the same time serves as a loosely fitting stopper for the wider tube. A smaller glass (a test-tube of 4 c.m. in length) containing the substance to be analysed, is let down into the bottom of the second tube by means of a glass rod bent at its lower end into the shape of a ring, and thus supporting the smaller tube. During the heating, which lasts an hour, a current of dry chlorine is passed down into the innermost glass.

Per cent.

0.5004 lead chloride lost in weight	0.0008	grm.	=	0.0159
0.5108	"	"	0.0006	" = 0.0117
0.5054	"	"	0.0013	" = 0.025

These losses are so slight as to have no influence upon the result of the analysis.

It was also important to ascertain if bismuth chloride is quickly and completely volatilised in the sulphur-bath. To this end, I placed in the wider glass, along with a weighed quantity of lead chloride, a weighed quantity of bismuth sulphide, and heated it in the sulphur-bath whilst chlorine gas was introduced as before.

After the lapse of an hour, he weighed the small glass and found that the mixture had lost weight to the amount of the bismuth sulphide present, whence it followed that at this temperature bismuth chloride was completely

volatilised. As in an analysis the metals to be separated are generally in the form of sulphides, it was necessary to determine whether lead sulphide is entirely converted into lead chloride in a current of chlorine. A weighed quantity of lead sulphide was treated in the same manner, when it was soon found by the change in the weight that the lead sulphide was not completely converted into chloride, but that the mass was melted together and was only superficially attacked by the chlorine. It was therefore probable that the lead sulphide would be converted better at a lower temperature, as it was proved by experiment. The lead sulphide was first boiled for an hour in the xylol-boiler, and then heated for an hour in the sulphur-bath in a current of chlorine. After the heating in the xylol-boiler the weight of the lead sulphide = 0.2293 grm., increased by 0.0268 grm. If the conversion had been complete, the increase would have been 0.0374. The deficiency in weight of 0.0106 grm. was made up after heating for one hour in the sulphur bath; consequently, the sulphide was in this manner completely converted into chloride.

The attempt was now made to separate the two sulphides in this manner, heating first for an hour in the xylol-boiler, and then for another hour in the sulphur-bath. In a mixture containing 42.17 per cent of lead, there were found 42.09 per cent.

The result shows that the metals may be perfectly separated in this manner. — *Berichte Deutsch. Chem. Gesellschaft*, xxiv., No. 18, p. 3554.

ON THE FORMATION OF MAGENTA.

By B. GOLDBERG.

In a memoir on the influence of thiophene upon the colouration of the benzene derivatives, which appeared in the *Comptes Rendus* (cviii., 520), M. A. Bidet communicated the very remarkable observation that the mixture of perfectly pure bases (aniline, ortho-, and para-toluidine) free from thiophene, on heating with arsenic acid yielded mere traces of magenta; whilst the bases obtained from nitro-compounds, to which some thiophene had been added prior to reduction, yielded the same coloured mass as the ordinary aniline oil from reds.

Hence the formation of magenta would depend on the presence of thiophene derivatives, although in minimum quantities, which introduce the reaction, whether by an action of contact or in some other inexplicable manner. There were, however, serious difficulties in the way of Bidet's observation, since, according to the observations of V. Meyer, amido-thiophene is a very unstable body, which is resinified in a short time at common temperatures, and which therefore cannot possibly be present in commercial aniline, even if it had been prepared from a material rich in thiophene. That commercial aniline is, in fact, free from amido-thiophene is confirmed by its conversion into benzol free from thiophene by the process of diazotising. The nitro-thiophene added would therefore be destroyed on reduction and subsequent distillation, and could therefore exert no influence upon the reaction of the formation of magenta. Hence, a repetition of Bidet's experiments seemed interesting. This task was undertaken by the author at the request of Prof. V. Meyer. The pure bases were first obtained by Bidet's process from nitro-benzol and para-nitro-toluol, which had been freed from nitro-thiophene by repeated treatment with concentrated sulphuric acid; and secondly, from benzol and toluol free from thiophene.

1. Nitro-benzol and nitro-toluol were treated with concentrated sulphuric acid at a gentle heat until the sulphuric acid added no longer changed its colour, or until a specimen on treatment with alcoholic potassa no longer gave the very characteristic reaction of dinitrothiophene, and was then reduced in the ordinary manner. The bases were then twice fractionated, those from aniline being

collected at 184°, and those from para-toluidine at 197°. The mixture, when heated with mercuric chloride, yielded at once an intense violet-red melt, which was also obtained on heating with arsenic acid.

2. In order to be quite certain that the colouration, in view of the intense tinctorial power of magenta, was not due to traces of this body formed in its midst, the following experiment was performed, for which the bases were derived from pure benzol free from thiophene, and from toluol freed from thiophenes by repeated treatment with concentrated sulphuric acid. From the pure bases there was prepared a mixture of 2 mols. aniline, and 1 mol. para-toluidine; and of this, 0.9894 grm. heated in the oil-bath for one and a half hours to 180–200° along with 2.8 grms. mercuric chloride and 2 grms. (excess) of aniline. Simultaneously with this experiment, 0.9740 grm. of a similar mixture of the commercial bases were likewise treated in the same manner along with 2.8 grms. mercuric chloride and 2 grms. commercial aniline in excess. In each case there was obtained a splendid violet-red melt. Each melt was extracted with 100 c.c. of alcohol, and in each case a solution of a deep red colour was obtained. The better to compare the tones, 10 c.c. of each solution was diluted with 100 c.c. of alcohol. Both were almost identical, that from the pure bases having the purer tone.

After these experiments, Bidet's statement may be regarded as erroneous.

For experiments on a small scale, the process of preparing magenta by heating with the calculated quantity of mercuric chloride in presence of an excess of aniline may be strongly recommended. It yields scarcely any carbonaceous amorphous substances, which cannot be avoided in the arsenic acid, &c., methods. — *Berichte Deutsch. Chem. Gesellschaft*, xxiv., No. 18, p. 3552.

ON THE STABILITY OF THE PETROLEUM COMPOUNDS.

By H. N. WARREN, Research Analyst.

THE alkaline cyanides of potassium and sodium, regarded as organic compounds, may deserve rank among the stable compounds, inasmuch that they exist unchanged at temperatures that would speedily disintegrate all other organic compounds. But of all organic compounds none can be said to possess more tenacity than the hydrocarbons petroleum, paraffin, &c., which, whether existing in the liquid or solid condition are simply changed upon elevation of temperature into a more gaseous compound, retaining their former properties. For instance, if petroleum, boiling at a low temperature, be passed through heated tubes, it becomes fractionised into compounds boiling at temperatures in accordance with the temperature to which it has been subjected, until a red heat is reached, when a true gaseous hydrocarbon is obtained, burning with the ordinary luminosity of these compounds and capable of reducing certain metallic oxides when brought in contact with it at an elevated temperature, at the same time forming substitutional compounds with the elements bromine, chlorine, &c. Strange to say, the hydrocarbons of the following class, although somewhat readily changed by heat, further resist most stubbornly the most powerful oxidising agents. Few, if any compounds, can resist the oxidising influence of fused nitre, yet petroleum may be passed through this substance with impunity even when at a bright red heat, and collected unchanged. The liquid or more solid compounds, if heated in sealed tubes with fuming nitric acid, are practically unchanged; an instance of this may be recorded from the bursting of an iron tube containing the mixture that had been kept for four hours at a temperature of 600° F.; small quantities collected afterwards possessed all their former properties. The only oxidising agent of sufficient power is chlorochromic

acid; if a few c.c. of this substance be allowed to fall to the bottom of an ounce of water, at the same time a layer of petroleum be brought to play upon the surface, on now shaking the whole briskly, a most energetic action is at once apparent, the petroleum becoming changed into a semi wax-like substance melting at about 400°F . This substance has, as yet, not been sufficiently dealt with to ascribe to it a formula, but it is the author's intention to deal further with the compound when time permits.

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ON THE DETERMINATION OF THE MELTING POINTS OF MINERALS.*

PART I.—THE USES OF THE MELDOMETER.

By J. JOLY, M.A., D.Sc., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

(Continued from p. 18).

It is necessary before proceeding further to describe the form of meldometer used in determining melting-points in the manner just sketched out. The accompanying figure (Fig. 2) from a photograph shows the apparatus (made by Messrs. Yeates and Son) at present in use. It consists of a rectangular piece of slate, cut into the form shown, on which two forceps are affixed, one rigidly (the further one on the figure), the other so that it is free to rotate round a vertical axis at one extremity, beyond which it is prolonged by a fine flat spring of steel. When these forceps are parallel to one another the distance separating their jaws is closely 10 c.m. This is the length of platinum ribbon whose expansion is measured when making experiments. A small helical spring attached to the vertical axle of the movable forceps, and to the fixed piece which receives the upper pivot of this axle (this piece conceals it in the figure), serves to confer a *slight* tension on the platinum ribbon, in that it is set to turn the forceps clockwise on its axis. Thus, when the ribbon expands the forceps rotates a little clockwise. At the further extremity of the spring which prolongs this forceps, a small polished plate of gold is attached, and to meet the surface of this a gold wire, carried at the extremity of the micrometer screw seen on the figure, may be brought on advancing the screw. The point of contact of pin and plate is as nearly as possible at the same distance to the one side of the vertical axis of the forceps as the centre line of the ribbon is to the other, when the latter is in its proper position in the forceps. Thus, the expansion of the ribbon may be measured by the movement of the micrometer screw, if at each change of temperature we get the gold pin to touch the gold plate *exactly*. To effect this without troublesome observations matters are arranged so that the meeting of pin and plate closes a circuit in which a galvanometer and a Leclanché cell are included. The bed of slate insulates the screw and forceps, and connexions are made as on the diagram (Fig. 3). This is an extremely sensitive method of reading a small movement. The screw pitch is about the fourth of a m.m.; the micrometer head carries 100 parts. Half these last divisions may easily be read, that is to say, the $\frac{1}{200}$ th of a m.m., or less than the $\frac{1}{2000}$ th of an inch, a quantity approaching the limits of the highest powers of the microscope, and indeed little more than two wave-lengths of sodium light. This movement is equivalent to a change of temperature of about 1.5° centigrade. The micrometer screw must have a uniform thread and be reliable in its

readings, or error will, of course, be introduced, just as would be the case with a badly calibrated thermometer. To bring the current into the forceps two large binding screws (seen in Fig. 2) are provided. These are attached to copper straps passing beneath the slate bed, and communicate with the forceps. To insure good contact with the movable forceps an annular space around the axle is provided in the slate, into which a little mercury can be

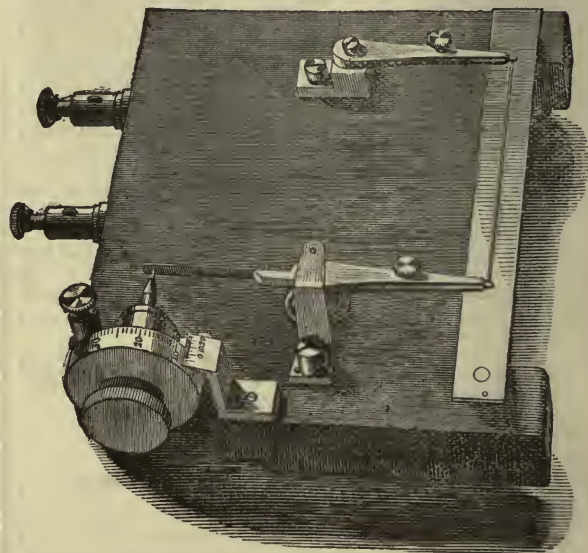


Fig. 2.

poured. A perforated wooden lid, loosely encircling the axle, keeps this mercury from accidentally being spilled out. The bottom of the mercury well is of brass, which receives the pivot of the axle on its upper surface, and at its under surface is screwed to the copper conductor. The forceps close by their elasticity, and are opened for the insertion of the ribbon by the small screws seen in the figure. A slip of polished brass, passing beneath the

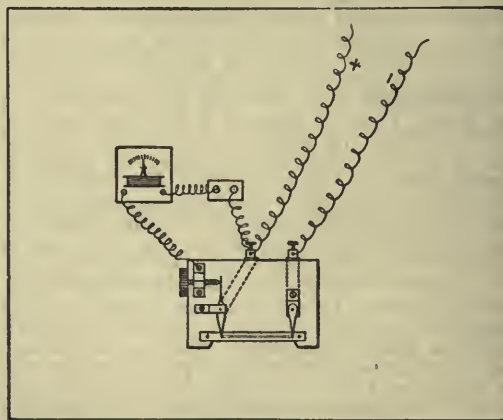


Fig. 3.

ribbon, serves to intercept heat from reaching the edge of the slate, and to receive chance fragments of substances falling off the platinum. The slate is cut back beneath this, for it is an object in the construction of this apparatus to preserve the slate from change of temperature. There seems but little heat communicated to the slate. I have not detected any sensible heating, even after prolonged experiments at high temperature. The co-

* A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

efficient of expansion of slate is so small that but little error can, I think, creep in in this way.

The platinum ribbon used in this apparatus is similar to that used in the first described form of the melder. The resistance of 10 c.m. of the ribbon, cold, is 0.43 ohm; when hot, rising to 1.5 ohms. A current of 6 ampères raises this length of ribbon to its melting-point. The ribbon is cut away at each end where fixed in the forceps, so that its section is reduced considerably where meeting the cold metal of the forceps. This adjustment is very important in this form of the melder. Any serious loss of heat by conduction from the ends of the strip produces an effect increasing with the temperature, not in a simple ratio, but more as the square of the temperature, the electrical



FIG. 4.

resistance being affected by the fall in temperature in such a way as to intensify the effect. Thus, the curve found for the extension will be affected; the curvature will tend generally to be diminished at high temperatures, and the position upon the ribbon we assign to the standard substances will also enter as a factor, for there will be inequality of temperature along the ribbon. A reduction of section to about one-fifth the full section will bring up the temperature at the ends sufficiently to reduce the error to a very small amount. It is easy to see, at a full red heat, how far the tint is uniform up to the forceps; but a more exact test may be made by reading melting-points within about 12 m.m. from the ends and at the middle, which should afford a difference not exceeding 5° C. at a dull red heat. It will be found

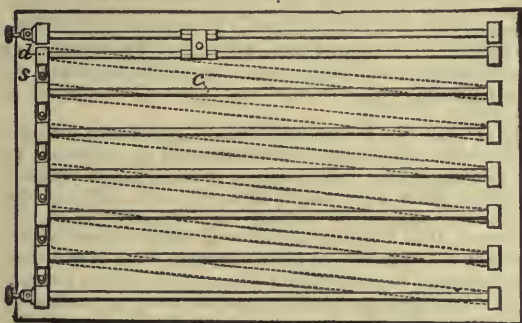


FIG. 5.

that if the ribbon be cut away with a scissors, and clamped as in figure 4, there will be sensible uniformity of temperature over the central 6 c.c. of the ribbon. I may observe that sometimes in the case of a ribbon very much cut away, and with a particular tension of the spring, keeping it stretched, a transverse vibratory motion of the ribbon takes place when it is heated. This is due apparently to air currents in the same manner as a flat body thrown into the air falls, with horizontal oscillations, from side to side. This vibratory motion, of course, renders vision indistinct. It may be stopped by bringing a fine platinum wire, fixed to a support, to touch the edge of the ribbon at its central point, but I have only occasionally noticed the phenomenon.

Before using a particular ribbon for measurements all traces of kink or bend are got out of it by raising it to a white heat for half a minute. In this connection it must be mentioned that the pull on the ribbon must be very slight, just sufficient to keep it stretched. A force equivalent to the weight of 1.5 grms. is sufficient. The ribbon I have found it best to use weighs 0.0073 gm. per c.m. run. The maker's number for this is 0.170. A less section is not advisable, as being too much affected by slight draughts. It is essential, of course, that the ribbon be of constant cross-section. There is some advantage in surrounding the ribbon by an open trough-shaped box of platinum foil from end to end. But while this conduces to steadiness in the temperature of the strip, it has the disadvantage of introducing a fresh difference of conditions towards the ends, except troublesome arrangements are made.* On the other hand, the amount of fluctuation obtaining in the case of observations made in a quiet room are small, and often not disadvantageous in observing the melting-point. Thus we observe the condition of the substance changing with these small fluctuations; and we set the micrometer so that the galvanometer needle is free when the substance shows the first signs of melting, and is deflected on the instant that solidification takes place. In this way the melting-points of non-viscous bodies can be caught with much accuracy. And I may observe here that, although some of Carnelley's observations (*Four. Chem. Soc.*, vol. i., 1876) appeared to indicate a considerable difference between the melting-point and the solidifying-point of many of the salts he dealt with, this difference is not substantiated by observations on the melder. The salt may generally be observed, with care, in such a state that the zone of liquefaction may be seen advancing from beneath, or retreating downwards at the least fluctuation of temperature. I think the method adopted by Carnelley for determining the point of the solidification was calculated to introduce an error due to radiation.

It is advisable not to assume that a curve plotted for one ribbon is suitable to another one which has replaced it, till we have verified a couple of points upon it, using such easily observed melting-points as are given in the sequel. Thus, if a speck of silver chloride, and of the black oxide of copper, CuO, be melted upon it, and finally a little palladium, we may assure ourselves upon this point. To avoid any chance of error due to the position of the substance upon the ribbon, no more than the central 6 c.m. should be availed of for determinations.

For the control of the temperature a higher resistance than that previously described is necessary. As the Rheostat I have in use is new in many particulars, and is very satisfactory, I think it well to describe it. It consists (Fig. 5) of eight rods of carbon, having a total resistance of about 4 ohms, fixed horizontally upon a board. Two of these are provided with a sliding cross-connection; the others may be, one by one, thrown into circuit, or cut out by a few turns of the screws seen at the front of the board in fig. 5. The raising of one of these screws, for example, permits a brass plate to spring out of contact with the underlying metal, and as the plate is cut out sufficiently to clear it of the shaft of the screw, connection is broken when the nut is raised, till it is no longer followed by the plate. The current then must traverse the carbon *c*, returning to the point *d* by the dotted connection. It is evidently possible to secure a perfect gradation of temperature by the use of this resistance, the travel of the bridge commanding a greater resistance than that of a single carbon. Thus if, when a certain number of carbons are in circuit, and the bridge has been moved to cut out the entire length of the two bridged carbons, we need still a higher temperature, we restore the bridged carbons to circuit by moving back the bridge, and then cut out one of the carbons, after which we begin again to advance the bridge so as gradually to cut out

* I have lately got over this difficulty, and the instrument as at present made is provided with a covering for the ribbon.

the bridged carbons. In this way we increase the temperature, nor is it necessary to take our attention from the microscope and the manipulations of the micrometer while making these changes in the resistance.

The diagram (Fig. 3) shows the convenient disposition of the apparatus when effecting measurements; the adjustable resistance being supposed inserted in the right hand lead. To observe the objects upon the ribbon a simple form of microscope, mounted on a bracket, projecting from a heavy base, is requisite. This can be moved along and directed to any point of the ribbon. One ribbon, of course, serves for many observations.

A principal advantage of this electrical method of reading the elongation of the ribbon is contained in the fact that so little of the observer's attention is called upon to effect this ordinarily difficult measurement. This is very important, for slight variations of temperature are continually occurring, due to draughts chiefly, and it is essential to be able to seize the reading at the moment the substance melts, especially in the case of bodies which flood out suddenly upon the platinum. The galvanometer needle may be observed simultaneously, with the object in the field of the microscope, if the head be raised a little above the eye-piece. The left hand is kept upon the micrometer screw, and at each small movement of the bridge (effected by the right hand), the elongation is followed by the micrometer, and the behaviour of the substance at the increased temperature observed.

(To be continued).

THE DETECTION AND DETERMINATION OF POTASSIUM SPECTROSCOPICALLY.*

By F. A. GOOCH and T. S. HART.

(Concluded from p. 24).

EXPERIMENT III. was made to discover the effect of the presence of a reasonable amount of sodium chloride upon the determination of the potassium. To a portion of the solution if pure potassium chloride containing 0.01 grm. of the element was added 0.1 grm. of sodium chloride taken from the salt purified as previously described. This solution was diluted and the comparison made with the standard according to the accompanying account.

Experiment III.

Volume of the test solution.	Characteristic of line compared with standard.
25 c.m.*	stronger
50 "	"
80 "	"
90 "	"
95 "	"
105 "	"
120 "	like
(120 × 0.0001 = 0.0120)	
Potassium found	0.0120 grm.
" taken	0.0100 "
Error	0.0020 "

The result of this experiment was most surprising; for, instead of diminishing the delicacy of the test, we find that the presence of a moderate amount of sodium chloride tends to increase the brilliance of the potassium line. The sodium chloride employed was a part of that prepared and tested as previously described and used in the experiments upon the qualitative determination of potassium. By no possibility could the 0.1 grm. of it taken in the experiment have contained more than 0.000001 grm. of potassium. It is evident, therefore, that the brilliance of

the potassium line gained 20 per cent in strength by the influence of sodium chloride, amounting to ten times the weight of the potassium present when the effect due to impurity of the salt could by no means exceed a hundredth of 1 per cent; that is to say, the observed effect is, at the very least, two thousand times greater than that which might have been conceivably produced by contamination of the sodium salt.

In the following experiment the effect of varying amounts of sodium chloride upon the spectrum of the potassium is shown. The sodium line was turned out of the field of view to obviate the dazzling effect of the sodium light, and a solution of potassium chloride containing 0.01 grm. of the element in 100 c.m.³ was examined spectroscopically after the addition of successively increasing amounts of sodium chloride, the strength of the line observed being brought into comparison with that produced by similar portions of the potassium solution containing no sodium.

Sodium chloride in a coil-full. M.grm.	Potassium in a coil-full. M.grm.	Ratio of NaCl: K.	Width of slit. M.m.	Characteristic of line compared with standard containing no NaCl.
0.002	0.002	1:1	0.18	like
0.010	0.002	5:1	0.18	"
0.020	0.002	10:1	0.18	a little stronger
0.040	0.002	20:1	0.23	much stronger
0.200	0.002	100:1	0.23	{ very much stronger
0.400	0.002	200:1	0.23	much stronger
0.600	0.002	300:1	0.23	"

From this it appears that the maximum strengthening effect occurs when the sodium chloride stands to the potassium in the ratio of 100:1. The apparent diminution of brilliance when the sodium is increased beyond that proportion is doubtless due to the effect of the strong light diffused through the field of view by the intensely bright sodium flame in spite of the fact that the line itself is cut off from direct vision.

The cause of the brightening effect of the sodium chloride we are inclined to attribute to the chemical action of the sodium dissociated in the flame. The effect of ammonium chloride, and of hydrochloric acid, in destroying the potassium light is well-known, and is due, presumably, in very large degree to the prevention of the dissociation of the potassium chloride. The dissociated sodium should naturally by its mass-action reinforce the disintegrating action of the heat upon the molecule of potassium chloride.

It is plain that the complication introduced into the quantitative spectroscopic determination of potassium by the presence of the sodium salt in the test can be obviated if it can be brought about that both the test and the standard solution shall contain the same amount of that reagent. It is a matter of interest, therefore, to discover whether it is possible to match sodium lines of considerable intensity so closely that the quantities of that element in solutions brought into comparison shall be practically equal, and so may be relied upon to give the same strengthening effect to the potassium spectrum. The following statement is the record of an attempt in this direction. The narrower slit was found to be best adapted to the comparison of the sodium lines.

NaCl in a coil full of new solution.	NaCl in a coil full of standard.	Width of slit.	Characteristic of line as compared with that of standard.
0.010 m.grm.	0.02 m.grm.	0.18 m.m.	weaker
0.017 "	0.02 "	0.18 "	weaker
0.019 "	0.02 "	0.18 "	weaker
0.020 "	0.02 "	0.18 "	like

The result shows the possibility of matching the sodium lines with a degree of approximation sufficient for the purpose in view; and, accordingly, a new standard solution was made containing 0.01 grm. of potassium taken

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlii., December, 1891.

Experiment IV.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 c.m. of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
30 c.m. ^a	0'23 m.m.	stronger	0'01 grm.	0'18 m.m.	weaker	108 c.m. ^a (a)	0'23 m.m.	weaker
70 "	0'23 "	"	0'03 "	0'18 "	"	108 "	0'23 "	stronger
100 "	0'23 "	weaker	0'05 "	0'18 "	"	109 "	0'23 "	weaker
			0'08 "	0'18 "	"			stronger
			0'09 "	0'18 "	"			like
			0'10 "	0'18 "	like			

(a) The test-solution having been accidentally over-diluted, its strength was increased by the addition of 0'0010 grm. of potassium, and this amount was added in the computation below to that originally in the test-solution.

$$(109 \times 0'0001 = 0'0109)$$

Potassium found 0'0109 grm.
 " taken 0'0110 "
 Error 0'0001 " = 0'9 per cent.

Experiment V.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 c.m. of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
40 c.m. ^a	0'23 m.m.	stronger	0'025 grm.	0'18 m.m.	weaker	160 c.m. ^a	0'23 m.m.	stronger
100 "	0'23 "	"	0'050 "	0'18 "	"	180 "	0'23 "	"
160 "	0'23 "	weaker	0'085 "	0'18 "	"	190 "	0'23 "	"
			0'100 "	0'18 "	"	200 "	0'23 "	"
			0'110 "	0'18 "	like	205 "	0'23 "	weaker
						210 "	0'23 "	"

$$\left(\begin{array}{l} 205 \times 0'0001 = 0'0205 \\ 200 \times 0'0001 = 0'0200 \end{array} \right) \text{ mean} = 0'02025$$

Potassium found 0'02025 grm.
 " taken 0'02000 "
 Error 0'00025 " = 1'25 per cent.

Experiment VI.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 c.m. of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
40 c.m. ^a	0'23 m.m.	stronger	0'045 grm. (b)	0'18 m.m.	weaker	110 c.m. ^a	0'23 m.m.	stronger
80 "	0'23 "	"	0'082 "	0'18 "	like	120 "	0'23 "	"
100 "	0'23 "	"				130 "	0'23 "	like
110 "	0'23 "	like						

(b) Originally present.

$$(130 \times 0'0001 = 0'0130)$$

Potassium found 0'0130 grm.
 " taken 0'0140 "
 Error 0'0010 " = 7 per cent.

Experiment VII.

Part I.			Part II.			Part III.		
Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.	NaCl in 100 c.m. of test-solution.	Width of slit.	Characteristic of sodium line as compared with standard.	Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
30 c.m. ^a	0'23 m.m.	stronger	0'05 grm. (c)	0'18 m.m.	weaker	100 c.m. ^a	0'23 m.m.	stronger
90 "	0'23 "	"	0'07 "	0'80 "	"	120 "	0'23 "	"
100 "	0'23 "	weaker	0'09 "	0'18 "	"	130 "	0'23 "	"
		like	0'10 "	0'18 "	like	140 "	0'23 "	weaker
					stronger			

Second.

Volume of test-solution.	Width of slit.	Characteristic of potassium line as compared with standard.
120 c.m. ^a	0'23 m.m.	stronger
140 "	0'23 "	"
150 "	0'23 "	weaker
160 "	0'23 "	"

(c) Originally present.

First.

$$(140 \times 0'0001 = 0'0140)$$

Potassium found 0'0180 grm.
 " taken 0'0150 "
 Error 0'0010 " = 7 per cent

Second.

$$(150 \times 0'0001 = 0'0150)$$

0'0150
 0'0150
 0'0000

in the form of the chloride, and 0.1 grm. of sodium chloride in 100 c.m.³, and with this new standard the following determinations were made. The experiment was performed in three stages; first, the test solution was diluted until its potassium line matched approximately with that of the standard; secondly, sodium chloride was added to the solution thus diluted until the sodium lines were brought to equality; and, finally, the test solution and the standard were again brought into comparison.

From these results it is plain that the sodium in test and standard may be matched closely enough to allow a fair approximation to be made in the determination of the potassium. In Experiments IV., V., and VI., no readjustment of the percentage of sodium in the final dilution, subsequent to the matching of the sodium lines, was attempted; in Experiment VII. this point was looked to, so that in this determination the strength of the sodium was kept equal to that found in the matching process. In Experiments IV. and VII. the matching of the sodium in the test-solution against that in the standard proved to have been exact; in V. an excess of 10 per cent was added, and in VI. the point of equality was thought to have been reached while there was still a deficiency of 25 per cent in the sodium chloride of the test-solution.

The error in the determination of the potassium in Experiment VI. may, perhaps, be accounted for by the mistake in matching the sodium; that of the first attempt in Experiment VII. we are disposed to attribute to lack of care in keeping the eye of the observer in the most sensitive condition, and of attention to the point of bringing the wires to the plane in quick succession. The largest absolute error met with amounted to 1 m.grm. in a total of 15. Though not accurate to the last degree when large amounts of potassium are to be estimated, the method, we think, offers some advantage without too great sacrifice of exactness in the determination of small amounts. In qualitative work the mode of manipulating described is exceedingly satisfactory. Aside from the practical application of the method the point which has been of greatest interest to us is the development of the fact that the presence of sodium salts in the flame is of direct influence in strengthening the spectrum of potassium.

THE GREENWOOD PROCESS FOR THE DIRECT PRODUCTION OF CHLORINE AND CAUSTIC SODA.

ON Wednesday, January 6th, we had the opportunity of inspecting this process, which is now being carried out in temporary works at Battersea. Mr. Greenwood, the inventor, has turned his attention to the electrolytic decomposition of common salt in connection with the extraction of gold from its ores by the chlorine process, and certainly, as far as we can judge from a necessarily brief examination, he has made a considerable step in the application of electric currents in industrial chemistry. The raw material operated upon is common salt, which is dissolved in water, and the brine, without any purification or filtration, is at once submitted to a current of about 4.4 volts and an intensity of 10 ampères per square foot of electrode.

The first difficulty to be overcome was to find a material for the anodes which should resist the action of nascent chlorine. The inventor has selected retort-coke, made up into plates and rendered impervious by a composition the nature of which is not made known. To increase the conductivity of the anode, and to give it greater firmness, it is provided with an iron core. This core is completely protected from contact with the chlorine by means of the composition just mentioned.

The next great difficulty is to prevent the chlorine and soda from recombining. For this purpose, Mr. Greenwood has devised a peculiar diaphragm; it consists of

slips of slate fixed horizontally like the laths of a Venetian blind, the interstices being filled with asbestos. If a mol. of chlorine impinges upon the slips, it could pass the diaphragm only by descending, and as its specific gravity is lower than that of the liquid, such a descent cannot take place.

The cathodes are made of cast iron, upon which caustic alkalies have practically no action. The liquid, after passing through a descending series of electrolytic troughs, is pumped back to be further submitted to the action of the current. The chlorine gas is at once conveyed away as liberated and passed into milk of lime, by which it is absorbed; or it may be applied to any other purpose as required. Thus it may be passed into lead chambers for the production of chloride of lime in the ordinary manner. This process being perfectly familiar to chemists is not shown in the experimental works now in action.

The caustic soda can, if needed, be converted into the solid form by evaporation, which is effected by the usual process. During this operation the common salt which has escaped decomposition—about 20 per cent, which would be very objectionable, *e.g.*, in the manufacture of soap—is eliminated by subsidence.

The production of caustic soda and of chlorine by this process is estimated by the inventor and by the experts who have been consulted to involve an economy of 50 per cent as compared with the present methods. If this calculation holds good on the large scale, and if no drawbacks reveal themselves, we may consider that the Leblanc alkali process is within a measurable distance of its end.

Mr. Greenwood has not as yet taken into consideration the question of the production of hydrochloric acid at a reduced cost. The cessation of the present supply of "tower salts" will be a serious affair in various chemical trades.

NOTICES OF BOOKS.

A Manual of Physics: Being an Introduction to the Study of Physical Science. Designed for the use of University Students. By W. PEDDIE, D.Sc., F.R.S.E., Assistant to the Professor of Natural Philosophy in the University of Edinburgh. Small 8vo., pp. 500. London: Baillière, Tindall, and Cox.

DR. PEDDIE gives in his preface a very good *raison d'être* for his work. He admits the importance of studying distinct treatises on the various branches of physics, as written by the most eminent *savants* of the day. But he urges that the student who follows this plan too exclusively may fail to get a complete view of "the essential unity and interdependence" of all these branches as it is evidently desirable. Too many of our investigators are, indeed, so immersed in the study of details that they forfeit the *esprit d'ensemble*. To counteract this defect is the author's object.

We doubt, however, whether he sufficiently appreciates the distinction between science and art. Thus, in his first chapter he writes, "the sciences of navigation and ship-designing, of energy, mineralogy, geology, meteorology, and so on, are purely physical sciences." Now, we submit that navigation, ship-designing, engineering, are not sciences but arts; mineralogy, geology, meteorology, &c., are sciences, part and parcel of the interpretation of the cosmos. Art tells us what to *do* in order to produce certain results; science tells us what *is*.

Dr. Peddie very justly insists that we have only two methods for obtaining accurate knowledge,—*observation* and *experiment*. Yet, in face of this incontrovertible truth, there are many persons in Edinburgh and elsewhere who seek to prohibit experiment as far as living matter is concerned. The remarks on the practical work

ing of the inductive process, on hypotheses and theories, will prove invaluable to the true student.

The chapters on the theory of contours and its physical applications, and on varying quantities, treat of subjects too generally omitted in our ordinary text-books of physics.

In the chapter on matter we note two interesting dicta. We read that matter devoid of all energy "most probably would not be matter at all in the sense in which we use the word"; and again, we know of the existence in nature of only a comparatively small number of elements. Into the origin of the elements the author does not enter. The chapters dealing with heat, light, electricity, and magnetism are characterised by great clearness, and will form a sound basis for the special study of any one of these subjects. As a whole the work must be pronounced highly satisfactory, creditable to author and publishers, and calculated to be useful to the readers for whom it is intended.

The Principles of Chemistry. By D. MENDELÉEFF. Translated from the Russian (Fifth Edition) by GEORGE KAMONSKY, A.R.S.M., of the Imperial Mint, St. Petersburg. Edited by A. J. GREENAWAY, F.I.C., Sub-Editor of the *Journal of the Chemical Society*. In Two Volumes, large 8vo., pp. 611 and 487. London: Longmans, Green, and Co.

WE have not yet quite completed our survey of the German edition of Prof. Mendeléeff's great work, translated by L. Jawein and A. Thillot, now appearing in parts.

As a matter of course, the two versions are substantially identical. The English edition now before us does not contain—as the preface informs us—two notes referring to the meaning of Russian words, and a description of the water of the streams near Petersburg, of merely local interest. On the other hand, it is enriched with three important appendices. The first of these is a reproduction of Prof. Mendeléeff's lecture delivered at the Royal Institution of Great Britain, on May 31st, 1889, being "An Attempt to Apply to Chemistry one of the Principles of Newton's Natural Philosophy." The author, setting out from Newton's third law of motion, shows that it is possible to preserve to chemistry all the advantages arising from structural teaching without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The third Newtonian law is, in fact, the great principle of substitution which since the middle of the century has led to such triumphs in chemistry, and from which still higher results are to be expected.

Appendix II. has for its subject the "Periodic Law of the Chemical Elements," and is the "Faraday Lecture" delivered by Prof. Mendeléeff, on June 4th, 1889, before the Fellows of the Chemical Society. Here the illustrious Russian *savant* develops his polemical attitude towards the concept of a primary material or *protyle* and against the origin of the elements by a process of evolution. He urges that evidence, whether experimental or theoretical, is wanting. It is very true that we have never seen, e.g., nickel converted into cobalt or *vice versa*; but no more have we seen the zebra converted into the quagga. Both these animals are now concluded to have sprung, not the one from the other, but from an earlier less specialised type. Just so with the nickel and cobalt, or with other closely allied groups of elements.

As for theoretical or speculative evidence, the periodic law renders it impossible to conceive of any other manner in which the elements can have originated, unless we embrace—as Prof. Mendeléeff appears *not* to do—the idea of a distinct special creation for each.

Appendix III., taken from the *Journal of the Russian Physico-Chemical Society*, vol. xxii., 1890, No. 8, discusses the epochal discovery of Th. Curtius, the formation of hydro-nitrous acid, otherwise known as hydrogen

nitride, azoimide, nitrohydric acid, N_3H . The possible existence of this compound Prof. Mendeléeff alleges that he had foreseen. For the composition of these bodies, N_3H and N_4H_4 , he refers to "one of his unpublished notes, dated 1871 or 1872;" though he admits that the announcement is of less importance than if it had been made previous to the publication of the memoir of Curtius (*Berichte Deutsch. Chem. Gesellschaft*, xxiii., p. 3023).

The author's remarks on the part to be played in education by the study of science, and especially by that of chemistry, are admittedly opportune and suggestive. He tells us—and would our heads of colleges, &c., could feel the truth and the value of his words—that "we are compelled to cast aside classical illusions, and to engage in a work which not only gives mental satisfaction, but is also practically useful."

"Knowing how contented, free, and joyful is life in the realms of Science, one fervently wishes that many would enter their portals." But how different is the career of the student seeking to widen the domain of human knowledge from that of the victim seeking mainly to pass!

Says Prof. Mendeléeff: "The time has come to turn away from visionary contemplation, from platonic aspirations, and from classical verbosity, and to enter the regions of actual labour for the commonweal, and to prove that the study of science is not only an excellent education for youth, but that it instils the virtues of labour and truth."

We have no hesitation in saying that the present edition is much preferable to the version of Jawein and Thillot. We think no one ought to enter upon the philosophy of chemistry without having prepared himself by a careful study of the work before us.

CORRESPONDENCE.

PAYMENTS ON RESULTS.

To the Editor of the Chemical News.

SIR,—The changes which will be introduced into the scale of payments for science instruction by the Science and Art Department next year amount almost to a revolution; but while the scale of payment is to be completely changed, with a view, apparently, of cutting down the grant, the system on which the payments are based remains the same.

Surely the time for payments on results has now passed. Admitting that as a temporary expedient for giving a stimulus to science teaching, and enabling classes to be started in places where otherwise it would have been impossible, it was useful and served its purpose. Its time has now passed, and we have reached a condition when it has not only ceased to be useful, but has become highly injurious to the best interests of science.

In all large towns there are now organised science and technical schools, where instruction is given in science, and which depend to a large extent on the government grant for their income. The instruction in most of these institutions is good, but it might be made much better if the students had not all to be put through the examination mill in order to obtain grant.

The teaching in technical schools is therefore kept at a low level, and its efficiency much impaired by the system of payment on results. But this is not all. Any person holding a "first class advanced" certificate in any one subject of science may teach that subject, and no objection will be raised to his starting a class if he can get a committee formed. As a result, school teachers who hold a certificate very frequently start evening classes at their schools. In many towns the School Board provides the room, gas, and apparatus, and the teacher takes the grant. The teaching is often of the poorest description, and the classes are run at very low fees, lower than is

possible at the regularly organised schools, where the teachers are more highly qualified, and therefore have to receive fairly good salaries; and not unfrequently the teacher offers a prize to each student who passes the examinations, that is, he gives the student a proportion of the grant earned. Young men commencing a study of science do not know the difference; to them "certificated science teacher" seems quite sufficient qualification, and the low fee is an inducement, so they too often go to the cheaper class. Hence the system encourages science classes, but certainly does not encourage good science teaching.

Then, again, we have day schools, often calling themselves technical schools, which, on examination, will be found to be based entirely on the Science and Art Department syllabuses, and where lads who ought to be finishing their general education are being crammed up in all branches of science to pass the examinations and earn grants.

Surely the time has come for a change; there is great need for government help for technical and scientific education, but it should be given in a rational way. The starting of evening classes by individual teachers or in schools should be prohibited in all districts where organised technical schools exist. The organised schools should be helped not by payment on results but by a grant, according to the work being done. Let the department appoint representatives on the governing bodies of the colleges in proportion to the amount of money paid; let inspection be as rigorous as possible to see that sound instruction is given; but let it be by practical men of science, not by military officers, often ignorant of science; and do away with the May examinations altogether; then we might have a system of science teaching of which the country might be proud, and which would give really good results.

As a teacher of many years' experience, both of day and evening classes, I am convinced that the examinations do no good, but a vast amount of harm to teacher, student, and institution. Much good work has been done in classes in connection with the department, but it has been in spite of, not on account of, the examination system. Teachers look upon the examinations as unmitigated evils, but have to put up with them because the grant must be earned.—I am, &c.,

A. HUMBOLDT SEXTON.

Glasgow and West of Scotland
Technical College, Glasgow.

THE NEW METHYLATED SPIRIT.

SIR,—There already exists one way, and so far as I know only one, whereby users of methylated spirit may still obtain it unadulterated with paraffin. Apply to the supervisor of the district for permission to purchase the spirit in quantity, direct from the manufacturers. The applicant will be required to specify the objects for which he proposes to use the spirit, and his statement and application will go to head-quarters. After the usual business of red tape and circumlocution, it will probably be allowed, and the applicant will then be required to find one surety in a bond for £200 as a safeguard against the application of the spirit to any improper uses. For this bond five shillings is charged. After these formalities are complied with, the holder of the permission is supplied with forms of requisition, and can order direct from the distillers. He also becomes a "user" of the spirit within the meaning of the recent order, and is entitled to requisition supplies free from paraffin. This is my own case, so that I can vouch for the correctness of my statements.

The method of procedure is roundabout and cumbersome, but it is apparently the only one whereby exemption can be obtained from the insane regulation which threatens to entail such disastrous consequences on British Science and Commerce. It is a marvel to me

how the chemists of the Revenue Department could ever have excogitated and recommended an adulteration which, as they must have been aware, would have the effect of rendering methylated spirit practically useless in the laboratory. The matter should not be allowed to rest until this regulation is rescinded. Our laws are, indeed, fearfully and wonderfully made; and it is hardly strange that British science should show signs of languishing under its many discouragements.—I am, &c.,

BRYAN CHARLES WALLER, M.D., F.I.C.

Masongill House, Cowan Bridge,
Kirkby Lonsdale, Jan. 11, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxliii., No. 26, December 28, 1891.

Researches on the Application of the Measurement of Rotatory Power to the Determination of Combinations formed by Aqueous Solutions of Sorbite with the Acid Sodium and Ammonium Molybdates.—D. Gernez.—The author has previously shown that mannite, in contact with certain acid molybdates, undergoes an action which is revealed by a considerable change in the value of the rotatory power. The increase is so great that the reactions produced in the aqueous solutions of these bodies may be traced by the action upon polarised light. Sorbite, an isomer of mannite, admits of researches of the same nature.

Metallic Borates.—H. Le Chatelier.—The author considers that the only borates whose formulæ are established beyond dispute are the two hydrates of boric acid, BO_3HO and $\text{BO}_3\cdot 3\text{HO}$. The alleged compounds, $4\text{BO}_3\cdot 3\text{MgO}$, $3\text{BO}_3\cdot 2\text{MgO}$, and $2\text{BO}_3\cdot \text{SrO}$, are mixtures.

Isomeric States of Chromium Sesquisulphate.—The solid green sulphate, $\text{Cr}_2\text{O}_3\cdot 3\text{SO}_3\cdot 11\text{H}_2\text{O}$, although having the same composition as the violet sulphate, must have a constitution completely different. It does not behave like an ordinary salt, not admitting of double decomposition. It is probable that the chrome is involved in a radicle possessing a certain stability. On decomposing this salt with an alkali, there is precipitated, not the normal chromium hydrate, but a hydrate which takes up only 2 mols. of water.

Silicon Chlorosulphide.—A. Besson.—This compound, $\text{Si}_2\text{Cl}_2\text{S}_2$, is obtained by the limited action of chlorine upon silicon sulphide at bright redness.

New Crystalline Copper Phosphide.—M. Granger.—These crystals answer to the formula Cu_3P . If heated to redness in contact with air they are transformed into phosphate. They dissolve easily in hot nitric acid.

Solution of Antimony Chloride in Saturated Solutions of Sodium Chloride.—H. Causse.—Solutions of SbCl_3 precipitated by an alkaline carbonate may be rendered quite clear again by the addition of an excess of sodium chloride.

A Double Copper and Ammonium Cyanide.—E. Fleurent.—The double cyanide is stable; if dissolved in ammonia it takes a blue colour on exposure to the air; it is insoluble in cold water, and slightly soluble in boiling water, without change. Above 100° it loses ammonia, ammonium cyanide, which sublimes, and there remains cuprous cyanide.

Thermic Study of Bibasic Organic Acids: Influence of the Alcohol Function.—G. Massol.—The introduction of the alcohol function in an adjacent carbon deter-

mines a notable increase in the number of calories disengaged at the moment of the formation of the salts. In the succinic series, the number of calories disengaged increases with the number of alcoholic hydroxyls. In the same series, the increase bears entirely upon the first acidity; the addition of a second mol. of base liberates the same quantity of heat for all acids.

Disodium Glycol.—M. De Forcrand.—This paper is not adapted for useful abstraction.

Action of Dilute Nitric Acid upon Mononaphthene.—M. Konovloff.—The principal product has the composition $C_9H_7NO_2$. With nitrous acid it gives a pale green colouration, due, perhaps, to the formation of a pseudonitrile.

Formation of Acetylene at the expense of Bromoform.—P. Cazeneuve.—Bromoform, in contact either with silver powder or with moist zinc-copper, is an abundant source of acetylene.

Action of Phosphorus Perchloride upon the Methyl-naphthylacetones: Naphthylacetylenes, α and β .—J. A. Leron.—The author has prepared the two naphthyl acetylenes, which had not been previously isolated, and which he now describes. The α -compound is a liquid boiling at $296-298^\circ$. The β -compound is a solid, fusible at $51.5-52^\circ$.

Observations on a Paper by Arm. Gautier and R. Drouin.—Th. Schloesing, jun., and Con. Laurent.—The authors consider that their results are somewhat obscured by the paper of MM. Gautier and Drouin. They have not announced, but demonstrated, the fixation of free nitrogen by inferior green plants.

—
Zeitschrift für Analytische Chemie.
Vol. xxx., Part 4.

Heating Appliances for Laboratory Use.—A number of devices by G. Barthel (*Helfenberger Annalen*). G. Barthel's benzene-burner (same source); Swoboda's petroleum lamp (*Pharm. Zeit.*); Bevington H. Gibbins's oil-gas lamp (*CHEMICAL NEWS*); paraffin-gas in laboratories by F. W. Boam (*CHEMICAL NEWS*); gasoline muffle-furnace by E. R. Ellis (*Four. Soc. Chem. Ind.*); improved spirit lamp, M. T. Lecco (*Chemiker Zeitung*); combination of three gas-burners, F. W. Branson (*Four. Soc. Chem. Ind.*); improved Bunsen-burner, L. Reimann (*Zeit. Angewandte Chemie*); further improvements by J. R. Griffin (*Four. Soc. Chem. Ind.*); universal burner, A. Stutzer (*Zeit. Angewandte Chemie*); improved gas-lamp, Max Gröber (*Zeit. Angewandte Chemie*); burner for heating water-baths; the Dessau gas-works (*Zeit. Angew. Chemie*); heating-worms, F. Lüttke (*Chemiker Zeitung*); evaporation apparatus, F. E. Ray (*Four. Soc. Chem. Ind.*).

Potash Apparatus for Ultimate Organic Analysis.—A. Delisle (*Dingler's Journal*).—This apparatus cannot be described without the accompanying figure.

Apparatus for Extraction.—A number of appliances are here briefly described, for accounts of which we must refer to the original.

Distillation of Mercury in a Vacuum.—W. Dunstan and T. S. Dymond.—(*From the Philosophical Magazine*).

Renovation of Caoutchouc Articles.—(*Central Zeitung für Optik*).—The articles are steeped in a mixture of two parts water and one part ammonia. In a few minutes, or at most in half an hour, they recover their elasticity.

Inferior Filter Papers.—L. Padé.—In an average sample of ordinary white filter paper the author found 10.4 per cent of ash.

Table of Specific Gravities of Aqueous Nitric Acid.—G. B. Squires.—(*From the Pharm. Era*).

Preservation of Aqueous Sulphuretted Hydrogen.—A. J. Shilton.—(*From the CHEMICAL NEWS*).

Influence of Nitrous Acid upon the Specific Gravity of Nitric Acid.—R. Hirsch (*Chemiker Zeitung*).—Each per cent of nitrous acid raises the specific gravity of the nitric acid by 0.01.

Recovery of Silver Residues.—H. Hussenot.—If such residues are in solution they are mixed with ammonia in excess, and from this ammoniacal solution the silver is precipitated by the immersion of a piece of copper. If the residues are insoluble in water and ammonia, they are first boiled with sulphuric acid. Chlorine, bromine, &c., are expelled, and copper sulphate is formed, which is rendered alkaline, and the silver is precipitated with copper. The silver thus obtained may be used for the production of silver nitrate. The ammonia and sulphuric acid need not be pure.

The Use of Oxycellulose for Analytical Purposes.—The power of oxycellulose to attract and fix colouring matters and in general bases (even from saline solutions), induced MM. Witz and Osmond to ascertain whether this attraction might not be applied for the detection and determination of small quantities of the substances precipitated in this manner. The authors have first occupied themselves with the determination of vanadium, and have found that it can be precipitated in this manner. In order to conclude as to the quantity of vanadium, they use it for the production of aniline black, and compare the intensities of the shades produced under corresponding conditions.

The Preparation of Pure Phosphoric Acid.—A. Joly.—(*From the Bulletin de la Société Chimique*).

Oxidation of Sulphides by the Action of the Electric Current.—E. Hintz.—An illustrated memoir from the *Journal of the Franklin Institute*.

Separation of Iron from Cobalt, Nickel, and Manganese.—Alonzo C. Campbell.—(*From the Journal of Analytical Chemistry*).

Determination of Arsenic in Iron.—F. W. Boam.—(*From the CHEMICAL NEWS*).

A Novel Fatty Acid.—A. Gérard.—(*From the Comptes Rendus*).

Qualitative Recognition of Glycerin.—C. A. Kohn.—(*From the Journal of the Society of Chemical Industry*).

A Sensitive Reaction for Tartaric Acid.—Ed. Mohler.—Already noticed.

Determination of Nitrogen.—A number of improvements in the known processes by Berthelot (*Soc. Chim.*); Buchan (*CHEMICAL NEWS*); Aubin and Quenol (*Soc. Chimique*); J. A. Müller (*Annales de Chimie*); improvement in the Kjeldahl process, R. Meldola and E. R. Moritz (*Four. Soc. Chem. Ind.*); comparison of the methods of Dumas, Wanklyn, and Kjeldahl, by Oddy and Cohen (*Four. Soc. Chem. Ind.*).

Basicity of Organic Acids.—D. Berthelot.—(*From the Comptes Rendus*).

Determination of Acetic Acid in Acetone, Vinegar, &c.—J. A. Wilson.—(*Four. Soc. Chem. Ind.*).

Determination of Aniline and Monomethylaniline.—F. Reverdin and Ch. de la Harpe.—Already noticed.

Determination of Free and Combined Acid in Hydrochloric Solutions of Hydroxylamine.—J. A. Müller.—According to the author, there is required only a simple titration with alkaline carbonate, using phenolphthalein as an indicator. Free hydroxylamine has no action upon phenolphthalein. The same holds good with the amines.

Determination of Sugars with Solution of Copper-Potassium Carbonate.—H. Ost.—(*Berichte Chem. Gesellschaft*).—The author has already discussed the determination of inverted sugar, of dextrose, levulose, galactose, arabinose, and lactose, and now takes up maltose. This sugar reduces much less cuprous oxide

than do the monosaccharides, and about half as much as inverted sugar.

Determination of Methoxyl and its Special Applications.—Extracts from the *Chemiker Zeitung* and *Monatshefte für Chemie*.

Determination of Lignine in Woods.—R. Benedikt and M. Bamberger (*Monatshefte für Chemie*).—Already inserted.

Examination of Chinese Tea.—P. Dvorkovitch (*Berichte Deuts. Chem. Gesell.*).—This memoir will be inserted in *extenso*.

Contributions to the Chemical and Microscopic Examination of Coffee and its Adulterants.—C. Cornauth (*Mittheilungen aus dem Pharm. Institut der Universität Erlangen*).—No particulars are given.

Rapid Volumetric Determination of Metallic Zinc in Zinc-Powder.—F. Weil (*Bull. de la Soc. Chimique*).—Already inserted.

Examination of Commercial Picric Acid.—A. H. Allen.—(From the *Four. Soc. Dyers and Colourists*).

General Process for Examining Fatty Lubricants.—L. Archbutt.—(From the *Four. Soc. Chem. Ind.*).

Determination of Mercury in Poisoning Cases.—Ludwig (*Zeit. Apotheker Vereins*).—Already inserted.

The Atomic Weight of Cadmium.—E. A. Partidge.—(From the *CHEMICAL NEWS*).

Revue Universelle des Mines et de la Metallurgie.
Series 5, Vol. xv., No. 3.

This issue contains no chemical matter.

MISCELLANEOUS.

Detection of Paraphenetidine in Phenacetine.—L. Reuter.—The author finds the reaction of the poisonous paraphenetidine with solution of iodine as less sensitive than that with chloral hydrate.—*Zeitschr. Anal. Chemie*, xxx., Part 4.

Action of Isoamyl Iodide upon Trimethylamine in Aqueous Solution, in the cold in Equimolecular Proportions. Trimethylisoamylammonium.—H. and A. Malbot.—We might expect that isoamyl iodide would yield a quaternary ammonium with trimethylamine; but the activity of tri-isobutylamine is less than that of tri-isoamylamine for one and the same ether. Hence we cannot obtain a tetrabutylammonium iodide.—*Bull. de la Soc. Chim. de Paris*, vi., No. 10.

The New Methylated Spirit.—An eminent medical organ learns that in future half per cent of *wood naphtha* (*sic*!) is to be added to methylated spirit. Our contemporary imagines that the mixture will be "absolutely undrinkable,"—which is a mistake. He is aware that the new concoction will be unwelcome to photographers and others, but he thinks that in such a case their complaints should be disregarded. We hold, on the contrary, that an injury to research and to the organic chemical manufactures will be poorly compensated by a hindrance thrown in the way of a few desperate drunkards. It is not too much to say that the Act permitting the sale of methylated spirits is completely stultified by this most mischievous innovation.

Patent Law.—The *Chemiker Zeitung* makes mention of a decision given by the German Patent Office and confirmed on appeal by the Supreme Courts. A foreigner held a German patent for a machine for mincing meat. The patentee made large machines for butchers, &c., in Germany, but the small machines for household use he made abroad and exported them to Germany. This was

held to be a contravention of Section 11 of the Patent Law, and the patent has been cancelled. In Britain every alien may hold a British patent without any intention to carry it out wholly or partially in this country. Thus our patent system is made to keep trade out of the country instead of promoting its introduction.

On the Nature of so-called Actions of Contact.—E. Ritsert (*Chem. Centralblatt*).—So-called contact actions, as occasioned under certain circumstances by platinum sponge, wood-charcoal, glass-powder, &c., may be explained by the assumption that the mols. of the active body in question by their vibration modify the vibrations of the bodies submitted to contact, and thus effect their combination. Thus, *e.g.*, the mols. of hydrogen and oxygen on contact with the mols. of platinum undergo such a modification of their vibrations that they take place simultaneously, but in opposite directions; whereby, according to the hypothesis of Bjerkness, a chemical union may be effected. The effects of the ferments may be explained in an analogous manner.

MEETINGS FOR THE WEEK.

MONDAY, 18th.—Medical, 8.30.

TUESDAY, 19th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.

— Institute of Civil Engineers, 8.

— Pathological, 8.30.

WEDNESDAY, 20th.—Society of Arts, 8.

— Meteorological, 7. (Anniversary).

— Microscopical, 8. (Anniversary).

— Geological, 8.

THURSDAY, 21st.—Royal, 4.30.

Royal Society Club, 6.30.

Chemical, 8. "The Estimation of Oxygen in

Water," by M. A. Adams. "A Pure Fermenta-

tion of Manitol and Dulcitol," by P. F. Frank-

land and W. Frew. "The Luminosity of

Coal-gas Flames," by V. B. Lewes. "The

Magnetic Rotation of Dissolved Salts," by W.

Ostwald. "On the Dissociation of Liquid

Nitrogen Peroxide," by W. Ostwald.

Royal Institution, 3. "Some Aspects of Greek

Sculpture in Relief," by A. S. Murray.

FRIDAY, 22nd.—Royal Institution, 9. "The Composition of Water,"

by The Right Hon. Lord Rayleigh, F.R.S.

— Physical, 5. "On the Driving of Electromagnetic

Vibrations by Electromagnetic and Electrostatic

Engines," by Prof. G. F. Fitzgerald, F.R.S. "On

Supplementary Colours," by Prof. S. P. Thompson,

F.R.S.

SATURDAY, 23rd.—Royal Institution, 3. "The Induction Coil and

Alternate Current Transformer," by Professor

J. A. Fleming, M.A., D.Sc.

ERRATUM.—P. 13, column 1, line 9 from bottom, for "leader" read "reader."

THE CHEMICAL NEWS

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THE CHEMICAL NEWS.

VOL. LXV., No. 1677.

ON THE IODINE NUMBER FOR LARD OIL BY THE HÜBL METHOD.*

By REUBEN HAINES.

SEVERAL years ago the writer made a large number of examinations of various oils and fats by the Hübl method, including among them lard oil. Although several determinations of the "iodine number" for lard oil have been published, the writer thinks it worth while to put upon record the results which he had obtained.

Three samples of lard were first obtained, two of them directly from two lard factories put up ready for the market, and expressly stated to be pure articles; and the third sample from a farmer who was accustomed to serve the writer's family with lard. These lards were tested for purity by tests in use at that time, and all were passed as genuine and unadulterated. The two factory lards had a melting-point of 45° C., while the country lard was much softer and had a much lower melting-point (33° C. was found, but this was possibly 2° or 3° too low). The iodine numbers found for these samples of lard were as follows:—

Factory lard No. 1 (average of 3 tests) ..	62.30
" " No. 2 " 4 " ..	62.49
Country lard " 2 " ..	59.33

The oil was then pressed out of each sample separately in the laboratory by means of an ordinary hand drug press, the temperature of the room being regulated to an average slightly below 50° F., never exceeding 55° nor going below 45°, the time of year being favourable for that object.

The pressure of the screw was gradually increased to the utmost that the press was capable of producing.

The oils obtained from these lards did not chill or become turbid until about 45° F. The temperature maintained in the pressing and the "cold test" of the oil produced are identical with factory practice. On being submitted to the Hübl test these oils gave the following results for the iodine number:—

Oil from Factory lard No. 1 (average of 5 tests) ..	75.14
" " No. 2 " " ..	73.03
" " Country lard " " ..	70.01
Average for oil from both factory lards ..	74.01
" " the three oils ..	72.72

These oils contained free fatty acid equivalent to oleic acid 0.86 per cent, 0.49 per cent, and 1.35 per cent, respectively, a short time after the above iodine numbers were obtained.

A peculiarity noticeable which I am unable to explain is the fact that the country lard of low melting-point, and also the lard oil made from it, have lower iodine numbers than the other lards and the oils from them. Nevertheless, the tests were all made with equal care to avoid error.

The same two oils made from factory lards were recently tested by the modified Bechi test (omitting the rapeseed oil and amyl alcohol, and acidifying only very slightly with nitric acid), but no darkening of colour was produced after heating exactly fifteen minutes on a water bath. The sample of oil from country lard was lost, and was not tested in this manner. There had been but slight increase in acidity in the oils from factory lards.

A sample of prime lard oil was obtained from a reputable dealer, who guaranteed it to be strictly pure from their knowledge of the manufacturers of it. This oil was obtained at about the same time as the above mentioned samples of lard. On being tested by the Hübl method the iodine number was found to be 74.02 as the average of four consecutive tests. It was also examined recently by the above modified Bechi test, and it did not become darkened in colour. The rise of temperature by Maumené's test was found to be 42° C., the experiment being made in the manner recommended by Allen.

Recently, also, the iodine numbers for the oil made from factory lard No. 1 (same sample as tested before), and for the above mentioned sample of prime lard oil were re-determined with very great care in regard to the details of manipulation. The following results were obtained:—

Oil from Factory lard No. 1 (two consecutive tests) ..	72.34; 72.33
Prime lard oil (single test) ..	73.73

The difference from the former figures may have been largely owing to the fact that in these later tests greater care was taken to secure perfect uniformity of temperature during the experiments, and to have a large excess of iodine in the titration, about equal to the quantity absorbed by the oil. In the former experiments the titrations were made at the expiration of two to three hours; in the latter ones the time was extended to six hours. Three hours is, however, found to be sufficient for non-drying oils. In the last experiments a burette with a glass stopper at the top and a small hole for admission of air was used for the iodine solution instead of closing an ordinary burette with a cork as was done previously. A delicate thermometer was kept constantly almost in contact with the burette. Equal measured quantities of potassium iodide solution and of chloroform in the tests and blank experiments, and only the purest chloroform was used; in the last experiments chloroform of the grade used for inhalation in medical practice.

UPON CERTAIN CONSTITUENTS OF THE "NITROGEN FREE EXTRACT."

By W. E. STONE,
Purdue University, La Fayette, Indiana.

SOME study of the constituents of feeding-stuffs, reported elsewhere in detail (*Amer. Chem. Journ.*, xiii, 73; *Ber. d. Chem. Ges.*, xxiii, 3791), point to the presence in such materials of a distinct class of bodies which, so far as our analytical methods go, may and do pass unrecognised under the comprehensive head of nitrogen-free extract matter. These are the gum-like carbohydrates which upon hydrolysis yield the pentaglucofoses or pentoses, *arabinose* or *xylose*, as the case may be. By means of the furfural reaction, which is peculiar to these bodies and their derivatives, I have shown that many of our feeding-stuffs contain very appreciable quantities of the same, particularly those of fibrous or woody nature like hay, straw, bran, maize, brewers' grains, &c.

These bodies are practically insoluble in water and alcohol, but are extracted from tissues by heating with weak alkalies, and in the same way are converted into sugars (the pentoses) by treatment with dilute acids. In the course of an ordinary fodder analysis these bodies would therefore succumb to the operations directed against the carbohydrates, and would increase their apparent proportions in the material, whether determined indirectly as nitrogen-free extract or directly by their reducing effect after inversion. Agricultural chemists have recognised the desirability of some more definite knowledge of the usually large amount and widely differing

* *Journal of Analytical and Applied Chemistry*, Vol. v., No. 5.

bodies referred to broadly as nitrogen-free extract, and the same is equally true of the great variety of nitrogenous bodies which find no intelligent expression in the "crude protein" of analytical results. My studies of the pentoses and the bodies from which they are derived have been made with the desire to throw some light upon the first-named class.

While recognising the varying character of the nitrogen-free extract, the most satisfactory disposition heretofore made of it has been to consider it as a whole, of carbohydrate nature, and upon this basis has been developed the current views with regard to the digestibility of foods, digestion coefficients, nutritive ratios, and general valuation based on composition.

Doubtless very grave errors are comprehended in this system because of the non-recognition of the variable nature of those non-nitrogenous bodies which succumb to the action of dilute boiling alkalies and acids. In other words, the reactions upon which are based the specifications of the carbohydrates are far too general to serve as a basis for what is ostensibly so important a matter as a digestion experiment. The following examples will show the fallacy of this sweeping classification:—

Maize meal contains about 80 per cent of nitrogen-free extract, which is largely farinaceous, and as such is easily subject to digestion or other destructive action. Wheat bran which contains proportionally very little starch shows nevertheless about 65 per cent of nitrogen-free extract, which we are not justified in valuing like that of the maize, nor may we assume an equal degree of digestibility. Brewers' grains which have undergone a process of malting and brewing expressly intended to remove all bodies of the nature of starch and sugar, yield after all upwards of 50 per cent of nitrogen-free extract. If the bran or brewers' grains be subjected to the action of dilute acids, however, the resulting products will reduce Fehling's solution as if a true sugar were present. Approaching this fact from another direction we find that both bran and brewers' grains contain large amounts of those materials which upon inversion yield the pentoses.

Having recognised the existence of these different classes of non-nitrogenous bodies, have we any authority for ascribing to them equal digestibility or nutritive value? The data bearing upon the subject are very meagre. Prof. Kühn designates the mucilages and gums to which these bodies belong as of doubtful nutritive value ("Ernährung des Rindviehs," Ninth Edition, p. 60). Gorup-Besanez regards gums, mucilages, and pectin substances as not digestible in the strict sense ("Physiologische Chemie," Second Edition, p. 767). Indirectly the experience of Gudkow (*Zeitsch. für Chemie*, 1870, 360) throws considerable light upon the matter. Recognising in wheat-bran the existence of a peculiar body which resembled the true carbohydrates in yielding a reducing sugar, he endeavoured to isolate it from the true carbohydrates, and especially starch, by malting. Failing in this he caused bran to be fed to swine, and found that while starch and other carbohydrates were digested, the particular object of his study was not, that it passed through the digestive tract undestroyed; and from the dung of the animal he succeeded in preparing the inversion product, which resembled the ordinary glucoses, but was not identified. This indigestible portion of the nitrogen-free extract of bran was afterwards identified in part by Prof. Tollens and myself (*Liebigs Annalen der Chemie*, 239, 249), and wholly so by Steiger and Schulze (*Ber. d. Chem. Ges.*, xxiii., 3110), as one of the pentose-producing gums.

No digestion experiments bearing upon these bodies have been made, because, until within a short time, no methods for their recognition or determination have been available.

I have, however, tested the dung of animals for substances of this class with positive results. The manure of steers fed upon a diet composed largely of maize ensilage yielded an amount of furfural equivalent to 5 per cent or more of these bodies. Manure from the same animals a

a period when their diet was composed largely of dry maize fodder, yielded the equivalent of 7 per cent or more of these substances. It is, moreover, highly probable that these percentages are much too low, owing to the incomplete methods by which they were obtained. They serve to show, however, that these bodies resist digestive action to a good degree.

In the light of this it is impossible to resist the belief that the indigestible carbohydrates recorded as such in digestion experiments are to a large extent of this class, and that digestive action is more selective in its action than our analytical methods. That is, while we assume an equal value for a large group of materials, they do not show the same behaviour toward digestion, so that the undigested carbohydrates found in the dung of an animal may represent in the main only a particular class of the whole, and possess quite different nature and value from those which have been digested. As to the absolute digestibility of these bodies I hope to gain some light by direct digestion experiments, which methods now at hand render possible.

Also in this same connection, viz., the ability of these substances to resist destructive forces, it is of interest to note this occurrence in ensilage. Both maize and clover ensilage which was well preserved, but had undergone the usual fermentative changes largely destructive to the true carbohydrates, such as starch and sugar, were examined and found to contain appreciable quantities of the pentose gums.

We are therefore able to differentiate from the true carbohydrates in the nitrogen-free extract a group of bodies which are undoubtedly of less nutritive value than the former, and which are resistant toward digestive and fermentative action to an appreciable extent.—*Agricultural Science*, vol. v., No. 4, April, 1891.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Concluded from p. 28).

No notion has perhaps interfered more with the natural development of physiological chemistry, and consequently with the insight into the cause of the chemical difference of organisms and their germs and ova, than the tacit assumption that it is possible to apply at once the principles which hold good in the ordinary reactions of organic and inorganic chemistry to the chemical processes in the living cell, which take place in the smallest spaces generally at much lower temperatures and at higher tensions. Pflüger alone (as early as 1875) has in part set himself free from this prejudice and has recognised the "self-decomposition" of the mols. in living protoplasm.

The view, however, still appears universally prevalent that the chemical difference of living beings depends on the difference of chemical compounds and on their dissimilar arrangement in the tissues. But that such cannot be the case has been already shown in a universally valid manner, even without the deduction laid down in this memoir.

If, for instance, the difference of a mammal and a bird from a chemical point of view depended on the difference of the compounds capable of production from their bodies or their arrangement, then the difference of two mammalian species, sub-species, or sports, or even of two individuals of the same kind, must depend on the same causes. There must, e.g., be contained in the egg from which a cock is evolved different chemical compounds from one which yields a hen, and every pair of eggs from which a couple of hens issue must contain dissimilar chemical compounds, since no two chicks just escaped from the shell are identical. If we are willing to adhere to this conclusion we should refute the entire principle which has been set up, for a chemical compound is in the

spirit of chemistry always—theoretically at least—capable of being produced, and must therefore occur more than only once, otherwise it would be no chemical compound. Living individuals, no two of which are so closely identical as two lots of one and the same chemical compound, must therefore, since they exist only once, be distinguished from each other by something beyond dissimilar chemical composition.

This something beyond cannot be found in a different arrangement of perhaps identical chemical compounds, since the arrangement of the chemical compounds in every individual being changes continually, otherwise it would cease to live.

Nothing therefore remains but the inference that in every living being the manner in which the chemical processes take place in it—that is to say in its protoplasm—is unlike. It is unlike because the protoplasm is of all natural products by far the most impressionable, *i.e.*, the most dependent upon imperceptible outer influences, and on account of its smallness, which excludes the action of mass at the decisive place (in the capillaries), it is unable to react on one occasion exactly the same as on another. So long as it has not accommodated itself to exactly the same external conditions (which can never be effected) it must behave differently. Hence, however strongly heredity may tend to the production of stable states under conditions which differ relatively little, it is impossible that two identical individuals should ever be produced. They would have to originate without protoplasm, like two crystals of felspar, of which we may at least suppose that they are distinguished by nothing other than their duality.

But we need no proof that no living being arises without protoplasm, and that no twin is so similar to its cotwin as one crystal is to another. Hence, as we have long been convinced of the accuracy of these general considerations, we have directed our attention much less to them than to the especial consequences of the view here presented on the nature of the chemism in living protoplasm and its dependence on the nature of the organic elements, and we hope shortly to demonstrate experimentally that an artificial imitation of the morphological relations, which are realised in the protoplasm of the plant cell and of the animal cell, yields principally the same results as the organism, at least as far as certain biochemical processes are concerned.

Of a "vital force" there can then remain, from a chemical point of view, nothing at all.

ON THE DETERMINATION OF THE MELTING POINTS OF MINERALS.*

PART I.—THE USES OF THE MELDOMETER.

By J. JOLY, M.A., D.Sc., an Assistant to the Erasmus Smith Professor of Experimental Physics, Trinity College, Dublin.

(Concluded from p. 32).

The Eye-Piece Galvanometer.

To render it more convenient to observe the deflection of the galvanometer simultaneously with the melting of the substance, or whatever other phenomenon we are observing upon the ribbon, I use the following arrangement:—A small galvanometer coil, wound with fine wire and containing a freely pivoted magnetised needle, is affixed to the eye-piece of the microscope. Projecting from the needle at right angles to its length, and entering a horizontal slot in the eye-piece, is a fine index-hand. This moves across the margin of the field, being accurately in the plane of the image formed within the eye-piece by the lower optical train. Its motion is confined

to a small arc, the magnetised needle without being stopped by pins at either side. This renders it fairly dead beat. When no current is passing the needle points to the centre of the field under the influence of a small control magnet affixed to the coil. Binding screws enable this galvanometer to be circuited with the larger galvanometer, which stands upon the table, and the Leclanché battery. This is a *very* great addition to our power of effecting an accurate measurement.

Appearances of Melting.

The appearances which characterise melting vary according to the nature and properties of the substance. A viscous substance is seen to round its angles slowly, the smallest fragments going first. If the temperature is well over the softening point the process is rapid, and spreads from small to large fragments, the whole coalescing finally in pools upon the platinum. It is always possible in such cases to fix a temperature at which the substance decisively melts, and one at which prolonged heating seems hardly to effect it. But, as already observed, softening may occur at temperatures much below the earliest visible phenomena of melting.

In the case of substances which melt rapidly and recrystallise on solidification, it is easy to fix the melting-point very closely. In fact, the temperature may be so regulated that the small passing changes of temperature affecting the ribbon determine fusion or solidification; the result being that the salt appears as if vibrating between the solid and the liquid states, rays of crystallisation darting across its surface, or again melting at the edges. These bodies are very easily dealt with; the salts selected for calibrating the ribbon, *i.e.*, for the construction of the curve, are of this nature, as the carbonate and nitrate of potash, as well as potassium bromide. Silver chloride is also a salt of this nature, but it possesses also the peculiarity of changing colour when melting. Solid, it is a greenish-white, crystalline substance; melted, it is an amber-coloured liquid, deepening in colour with rise of temperature. The passage from the one state to the other is a well marked point. Similar phenomena mark the melting-point of silver sulphate. If the substance is a metal the melting-point is looked for in either of two ways. We may scrape a little dust off the metal on to the platinum ribbon, and, raising the temperature continually, catch the reading when the little fragments suddenly run down. A second trial, in which we may more carefully approach the melting-point, will fix a correct reading. In the cases of silver and palladium, we may observe the behaviour of a pool of the previously melted metal; when such is again just melting a change of colour of the surface is visible. The appearance is as if a red or yellow flush (according to the temperature) passed across the surface; it is very characteristic, and seems due to the smoothing of the rugosities on the solid substances which keep the surface darker by their greater area of radiation. Points determined in this way, in the case of silver and palladium, agree with the points determined by observation of the breakdown of very small scrapings of the metal. It is to be observed that metals should be determined only on the first or second melting, as there is risk of mutual solution or alloying with the platinum, which would affect the melting-point. In general, it may be said that the breakdown of very small fragments, or a rocking motion apparent in the larger fragments, are the readiest, and probably the surest, signs of melting.

Range of the Meldometer and its Degree of Reliability.

Coming now to the consideration of the range possessed by this apparatus for the comparison of melting-points—for such it obviously is—it will be convenient to refer to the curve of melting-points obtained by observations on the meldometer, such as I have described. The points fixed on the lower part of the curve are based, principally in the results of Carnelley (see his "Melting-

* A report read before the Royal Irish Academy, May 11th, 1891, and reprinted, with revision by the author, from the *Proceedings R.I.A.*, 3rd ser., vol. ii., p. 38.

and Boiling-Point Tables"), or the *résumé* of his results given in the *Physikalisch-chemische Tabellen* of Landholt and Bornstein. Carnelley and Williams's observations were made by a calorimetric method, in which they heated a platinum vessel to the temperature at which the salt melts, and plunging the platinum in water determined the quantity of heat contained in the platinum at the unknown temperature (Carnelley and Williams, *Journ. Chem. Soc.*, vol. i. (1876), p. 489). The specific heat of platinum had been measured by Pouillet, by direct comparison with the air-thermometer up to 1200° C. (Pouillet, *Comptes Rendus*, vol. iii. (1876), p. 782). The data so obtained are used by Carnelley. This physicist was so well acquainted with the whole subject that it appears hardly possible to say more in their support than that he was satisfied to accept them as the best basis available whereon to investigate and discuss the periodicity of the melting-points of certain groups of compounds.

Violle (*Comptes Rendus*, vol. lxxxv. (1877); vol. lxxxvii. (1878); vol. lxxxix. (1879), finding the variation of specific heat with temperature by reference to the porcelain air-thermometer, determined the melting-points of silver, gold, copper, palladium, &c. His determinations, therefore, rest on a similar basis to those of Carnelley.

The whole question has been recently reviewed very completely by Herr Carl Barus, for the U. S. Geological Survey. (*Bulletin* No. 54, 1889).

Assuming the reliability of Pouillet's investigations, there appears little doubt that, so far as Carnelley's observations extend (900° C., about), they are probably the most reliable yet made; although it is probable—almost certain, indeed—that there is a small minus error increasing with the temperature of melting (see account of his method *loc. cit.*). It is, perhaps, a further proof of their reliability that their agreement *inter se* appears very close. If we assume the co-efficient of expansion of platinum to preserve a fairly uniform value over this range we find, from observations on the maldometer, that his data closely lie along a common line. The agreement is still closer if we assume a slow, fairly uniform rate of increase of the co-efficient of expansion (*a priori* probable); and this assumption enables us, also, to extend the line, through the careful results of Violle, for the highest temperatures. Thus, silver 954° C., gold 1045° C., and palladium 1500° C. fall upon such a slow curve as is seen in the plate. Violle's results, which, as observed, are also calorimetric, and are admittedly of much value, are, in fact, singled out by Carnelley in his "Melting- and Boiling-Point Tables," as specially reliable. By using these points of Violle's we may extend our knowledge of the melting-points of minerals up to (and safely somewhat beyond) the temperature of 1500° C. with the same degree of accuracy attained in the research of Violle. Pure palladium is supplied by Messrs. Johnson and Matthey. Pure precipitated gold (1045° C.) should be used if this substance is experimented on. It is to be spread in fine dust upon the ribbon, and the moment at which the particles break down seized as the melting-point. I have found by interpolation upon the curve that precipitated black oxide of copper, CuO, melts at nearly the same temperature (at 1055° C.), and as this substance breaks down at once, I suggest it as a substitute, giving a convenient point upon the curve between silver and palladium. Its first breakdown must be observed, as upon re-melting phenomena occur which render the melting-point difficult to distinguish. Copper (1054° C.) is difficult to deal with owing to oxidation; on the maldometer it is hard to distinguish its melting-point from that of gold.

At the very highest temperatures the platinum ribbon reveals a certain amount of viscous stretching. It was very important to determine the amount of this, and its influence in setting a limit to the range of measurements. Observations were accordingly made in which the temperature was raised by different amounts, and the behaviour of the ribbon observed over intervals of five

minutes. Where viscous extension took place the ribbon, of course, did not return to its initial length. The true expansion in such cases was deduced by deducting from the whole extension the observed amount by which it failed to return to the initial length. From the extensions the temperature was computed as described, and the following table obtained:—

Temperature, ° C.	Duration of Heating.	Viscous Extension.
1430	5 minutes	0'0
1510	5 "	0'0002
1565	2 "	0'0004
1620	5 "	0'0010
1780 (?)	3 " (stretching rapidly)	0'0033

Length of ribbon closely 3'80 inches.

A viscous extension of 0'0001 introduces an error of about 3° C. It was observed, too, that at the temperature of melting palladium (1500°) a small viscous extension was sometimes apparent, and also upon prolonged exposure to the temperature of melting quartz. But it is evident that the error introduced by this effect, even if neglected, would not at a temperature so high as 1500° C. maintained for five minutes be a source of serious error. I think the allowance for it which can readily be made by reading the new length l_1 , after the observation, may be considered to eliminate its effects. Thus producing the curve beyond Violle's result for the melting-point of platinum temperatures so high as 1600° C. are determinable, and for their accuracy may with considerable assurance be referred to the degree of accuracy attained by Violle in his determination of the melting-point of palladium. So high as 1700° the results obtained with this apparatus will still possess an approximation to this same degree of accuracy.

Drawing the Curve.

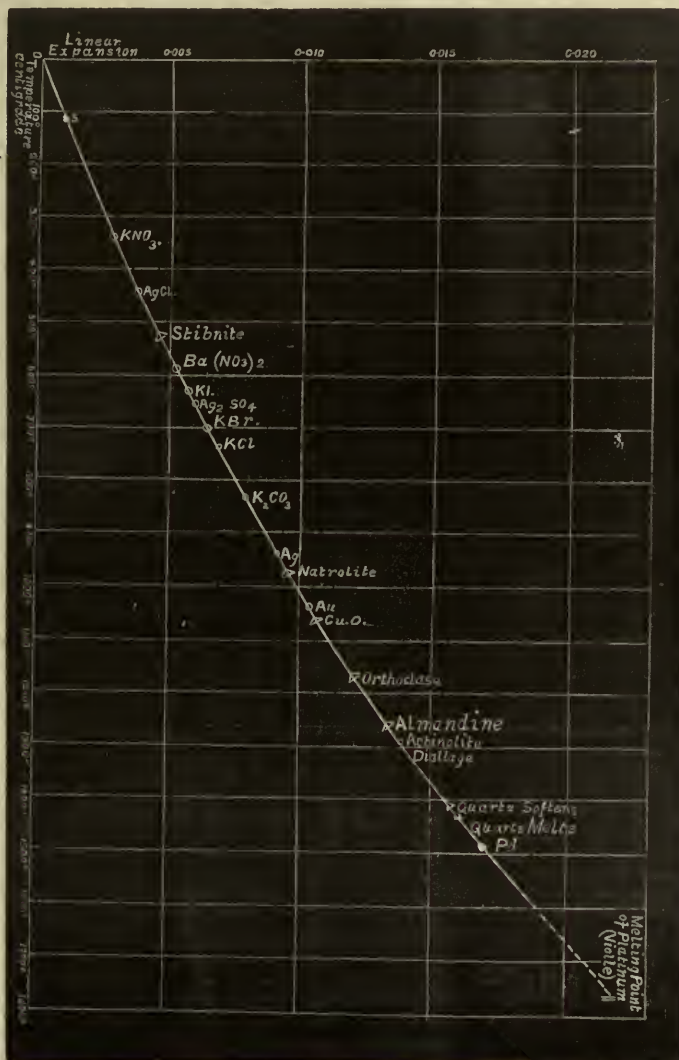
A single numerical example of the method of finding a point upon the curve may be of service. Thus, in the case of silver chloride, at starting we find the head of the screw reading 1098 divisions from the zero point, the temperature being 15° C.; when the salt is melting we find the head reads 1242 or the advance has been 144. Now each of these represents an advance of the 1-1000th of an inch, the thread being pitched 1-100", and the head carrying 100 divisions. We measure, when cold, the ribbon by a divider, and find it reads 3'80". In taking this measurement we are not particular to scale the exact whole length; for although the ribbon is cut away at the ends in the manner before described (to favour uniform heating), it is seen to remain dark where *quite* close up to the forceps. It therefore conduces to accuracy to read the length about 1-100th of an inch less than its full length. The correction is evidently a very immaterial one in any case from the comparative nature of the observations throughout. The fraction $l_2 - l_1/l_1$ has now the value $144/38000 = 0'00379$, which is accordingly plotted; conveniently to the scale 0'0001 to the m.m. This length is set off perpendicularly from the horizontal scale of temperature at the point 436° C. The melting-point is indeed given by Carnelley as 451° C., but the interval of temperature corresponding to the observed expansion is this value less the initial temperature of 15° C. This is the most convenient course to pursue if we wish to carry the curve through 0° C., which should be done if we desire to preserve it for continued use. Fifteen degrees higher up on the curve we may write AgCl, as is done on the drawing. In this manner the curve is constructed. An unknown temperature is evidently determined from an observed expansion by calculating the value of $l_2 - l_1/l_1$ corresponding to this expansion, and finding from the curve what temperature corresponds to such an ordinate. To this must be added a number of degrees corresponding to the initial temperature.

For determining the curve of melting-points, I have found the following substances convenient:—

	Degs. C.
Potassium nitrate.. .. .	339
Silver chloride	451
Silver sulphate	654
Potassium bromide	699
Silver	954
Gold	1045
Or cupric oxide (first fusion) ..	1055
Palladium	1500

For verification of a new ribbon it is sufficient to select silver chloride, gold (or cupric oxide), and palladium.

upon the curve of expansions in the same manner in which I propose that mineralogists should determine the melting-points of mineral bodies. It is seen that in the apparatus described the mechanical arrangements are such that there is no magnification of the expansion at the point at which the micrometer is applied. If it was desired to apply this form of platinum-thermometer to more minute measurements, as over a more limited range of temperature, it is of course easy to secure more delicate indications by lengthening the spring which prolongs the movable forceps, so that we exaggerate at the micrometer the extension of the ribbon, or by lengthening



The foregoing method enables us to determine in a few minutes the melting-point of a substance on the same basis of accuracy as that attained by the most careful observers. Only a very minute quantity of material is required, a condition often desirable in dealing with mineral bodies, and often again with bodies prepared by the chemist. Perhaps the peculiar function of the melder-meter will be best understood from the consideration that from any three or four of his numerous and laborious determinations, Carnelley might, by the use of such an apparatus, have at once arrived at the melting-points of the many other substances he dealt with, by interpolation

the ribbon itself. Thus doubling the length of the spring with the present dimensions of the ribbon secures a reading closer than one degree centigrade. The applications of such an apparatus—necessitating only the most minute quantities of substances for the determination of their melting-points—might be many in chemical research. On the other hand, however, it must be observed that it appears scarcely applicable to the determination of boiling-points, at any rate of volatile liquids, my limited experience in this direction indicating that the small quantity of the liquid is soon evaporated, and the indications of boiling difficult to catch.

EXPLANATION OF PLATE.

The points on the curve marked by circles are the melting-points of assumed reliability from which, with the readings of, the maldrometer for the expansion of the platinum ribbon, the form of the curve is determined. The points marked by triangles are melting-points found by the use of the curve so constructed.

ON A

RAPID METHOD FOR THE ACCURATE
RECOGNITION OF SULPHIDES, ARSENIDES,
ANTIMONIDES, AND DOUBLE COMPOUNDS
OF THESE BODIES WITH METALS.*

By CHARLES A. BURGHARDT, Ph.D., &c.

THE process to be described has been applied to the minerals mentioned below, but I have no doubt that all similarly constituted minerals will also be easily recognised by the method.

I am quite sure that all mineralogists have experienced much annoyance and difficulty in obtaining really satisfactory results with the ordinary blowpipe reactions in regard to some of the compounds of arsenic, antimony, and sulphur with metals, particularly in the separation of the metal or metals from the above-mentioned elements. In order to obtain the metal, the assay requires a most careful and tedious roasting on charcoal in the *oxidising flame* of the blowpipe, in order to volatilise away the sulphur, arsenic, or antimony. When this roasting is complete the residue (oxide) is mixed with either sodium carbonate, or that salt and cyanide of potassium, and fused for a considerable time on charcoal in the reducing flame in order to obtain a bead of the metal. Sometimes borax is used to eliminate a metal from a mixed oxide residue, dissolving one oxide and leaving the other. If the oxides left after the oxidising process above-mentioned are not soluble in borax, then the bead which is obtained in the subsequent reducing process is an alloy, and practically useless as a means of recognition of the metals entering into its composition. Having often been disappointed with the results obtained by the above-mentioned blowpipe processes, I determined to find, if possible, a more rapid and certain method of analysis of minerals.

The apparatus required is that which all mineralogists have been in the habit of using for a long period, viz:—

1. Small porcelain crucibles.
2. Test tubes.
3. A small platinum basin and a platinum crucible.
4. A platinum spoon made rather deep, something like a platinum crucible with a handle.
5. Hard glass tubing, closed at one end and about 4 in. long; a cork is placed in the open end, with a hole bored through it, and a hard glass tube of small bore passed just through the cork. The straight piece outside the cork is bent either *twice* at right angles (if required to pass vapours into water or solution), or *once* at right angles and drawn out to a fine nozzle if required to test for arseniuretted or antimonuretted hydrogen.
6. A Bunsen burner of the ordinary type, or a spirit lamp.
7. Funnels, beakers, porcelain evaporating basins, stir rods, &c., &c., and small pieces of clean sheet iron and sheet copper.

Reagents.

Ammonium nitrate	(solid)
Sodium nitrate	"
Potassium bisulphate	"
Metallic zinc	"

Hydrochloric acid	(solution)
Potassium ferrocyanide	"
Potassium ferricyanide	"
Ammonia liquor	"
Caustic soda	"
Silver nitrate	"
Stannous chloride	"
Bichromate of potassium	"

All the above reagents can be carried about in the dry solid condition for travelling, except the hydrochloric acid and the ammonia. With regard to the latter, it can be carried in the form of solid ammonium carbonate or ammonium sulphate; and the ammonia liberated from the respective salts in the usual manner, and passed either into the solution to be tested or else into water. I cannot at present give as easy a way of producing hydrochloric acid when it is wanted from dry materials, but think that it could be prepared in sufficient quantity by heating together in a glass tube (with delivery tube attached as described above) a mixture of potassium or sodium bisulphate and sodium chloride. Hydrochloric acid gas would then be liberated. Nitric acid is not required in this method at all.

Having thus briefly touched upon the present method of the treatment by the blowpipe of the minerals containing volatile elements, I will at once proceed to describe the method proposed by myself to attain the same object. The oxidising reagent I use is pure crystallised ammonium nitrate. This salt on being heated to about 250° C., decomposes, intumesces, and the products of its decomposition are nitrous oxide (N₂O) and water. *Thus the products are both gases, and nothing remains behind, which is certainly a very great consideration.* The nitrous oxide, at the high temperature used, rapidly gives up its oxygen to any element having an affinity for that gas, and oxidises it, so that finally the principal decomposition products of the original ammonium nitrate which are evolved as gases are nitrogen and vapour of water. The *modus operandi* is exceedingly simple. The mineral to be tested is crushed up and powdered into an exceedingly fine powder, a platinum or porcelain crucible is taken and filled to about one-fourth of its bulk with coarsely crushed ammonium nitrate crystals, then upon this about 0.5 grm. of the finely powdered mineral is placed, and the crucible and contents held with a pair of tongs over the Bunsen lamp, just in the flame. A violent reaction is at once set up, and care must be taken to withdraw the crucible from time to time from the lamp in order to avoid loss by boiling over the sides. Sometimes it is necessary to add some more ammonium nitrate crystals to the partially cooled "melt" in the crucible and heat again in order to complete the reaction. *An excess of ammonium nitrate cannot possibly do any harm, and it ensures success.*

The crucible having been allowed to cool, the contents are extracted with water and the solution separated from the insoluble matter. During the fusion of the mineral in the crucible, characteristic colours of various metallic salts are most distinctly observed; occasionally, therefore, the operator must watch this fusion closely. The fusion and lixiviation of the melt only occupy a minute or two when one has attained some experience, but the whole analysis need not exceed fifteen minutes even in complicated compounds. When melting the mineral in a glass tube with the ammonium nitrate, and passing the products of combustion into water, care must be taken to carefully dry the ammonium nitrate in a water oven previous to use, as it rapidly absorbs moisture from the air, and the water thus evolved in the fusion tube would cause the hot glass to crack. The thoroughly dried ammonium nitrate is conveniently kept in a well stoppered bottle.

Sulphides of Arsenic.

Orpiment (As₂S₃).

Realgar (AsS).

Fused in glass fusion tube with tube bent twice at right

* From the *Mineralogical Magazine*, Vol. ix., No. 43.

angles, the open end of the delivery tube dipping into water. Sulphuric acid was found in the water in distinct quantity by the usual barium chloride test; therefore the mineral was a sulphide. In the fusion tube was a slightly coloured solid residue which could be eventually completely dissolved in boiling water; it gave the reaction for arsenic acid (with nitrate of silver) and all the other reactions for arsenic; mirror on being treated with metallic zinc and acid potassium sulphate, and the arseniuretted hydrogen, decomposed into metallic arsenic by heating the hard-glass delivery tube to redness. *The mineral was therefore arsenic sulphide.*

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

December 17th, 1891.

Dr. W. H. PERKIN, F.R.S., in the Chair.

MESSRS. William A. S. Calder, Arthur Colefax, Charles E. Eastick, Henry C. Jenkins, and Thomas Neilson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Adams, Broomfield Place, Smethwick; Francis B. Darbishire, 59, Elienstrasse, Dresden; James Hendrick, Laurel Cottage, Watermoor, Cirencester; Henry Hollingshurst, 2, Jentha Road, East Hill, Wandsworth; Frank William Lucas, M.A., 183, Belle Vue Road, Leeds; Ernest John Parry, B.Sc., Brooklands, Bensham Manor Road, Thornton Heath; William Pullinger, 27, Queen's Road, Oldham; Charles F. Seymour Rothwell, 82, Manson Street, Manchester; Thomas John Buckler Sandercock, Sidcup College, Sidcup, Kent; Henry John Spray, 15, Bucharest Road, Wandsworth; Alfred James Squires, 16, Lower Road, Newark, Notts.

Of the following papers, those marked * were read:—

75. "The 'Gas-volumeter' and 'Gravitolumeter.'" By G. LUNGE (*cf. Proc. C. S.*, p. 168).

In the *Proc. C. S.* (No. 96, April 4, 1891), Professor Japp describes an instrument by means of which the observed volume of a single gas gives directly the weight of the gas. This instrument is based on the principle of reducing gases to a standard volume by means which are the same as those I first introduced in the "gas volumeter," but Professor Japp prefers to call it by another name "gravitolumeter." To this I objected in a brief note in the *Berichte* (xxiv., 1656), and Professor Japp has since replied in the last part of his full paper published in the *Transactions of the Society* (1891, lix., 894).

If it were merely a question of the name of an apparatus, I should not trouble the Society, as I have nothing to add to what I then said in the *Berichte*, leaving it to others to choose between the names in question. But in his answer to my objections Professor Japp has charged me with making contradictory statements and ignoring "a commonplace of physical measurement;" this compels me to ask the Society to publish my refutation of these charges.

In the *Berichte* (*loc. cit.*), I stated that the "gravitolumeter" is in point of fact absolutely identical with the "gas volumeter," but that by modifying the form of the regulator ("Reductionsrohr") which I prefer, Professor Japp has diminished the accuracy of the instrument. He remarks: "I fear I must leave Professor Lunge to reconcile these two statements." If he had referred to my original descriptions in the *Berichte* (dated February 14th, 1890) and the *Zeitschrift für Angewandte Chemie* (March 1st, 1890), he would have had no difficulty in doing so.

My regulator contains a certain volume of air, which

under "standard" conditions causes the mercury to rise to a fixed point, and by producing this condition simultaneously in the regulator and the gas burette, I reduce the gas contained in the latter to standard conditions also, thus avoiding in the measurement of the gas the necessity for observations of temperature and barometric pressure and all calculations connected therewith. My apparatus has completely realised this object, and Professor Japp has adopted the self-same principle and availed himself of the same means for effecting the reduction. It is manifestly indifferent, as far as the principle is concerned, whether the standard volume of air in the regulator is 25 c.c., or 50, or 100, as I have distinctly stated in a passage possibly overlooked by Professor Japp (*Ber.*, xxiii., 444, line 30). For the sake of obtaining more accurate results, I preferred in practice to take 100 c.c., and to contract the tube below this point, in order to get larger divisions, but I did not confine my apparatus to any such special form. On the contrary, I showed, even in my first communication, several modifications of the regulator (with cylindrical top, with bulb top, with tap, and with a capillary); I also said (*loc. cit.*, p. 444, line 24): "I quote, of course, these combinations, to be varied at will, merely as *examples* how the apparatus may be arranged," and in the *Zeitschrift für Angewandte Chemie*, 1880, pages 140 and 144, I remark that any "nitrometer (*a fortiori* any "gas burette") may serve the purpose of a regulator." Consequently, when he adopted for this purpose an ordinary 50 c.c. gas burette, Professor Japp did not introduce *any* modification in the principle of my "gas volumeter," but merely selected one out of the various forms which would at once occur to any chemist on reading my description, although certainly not that which admits, in my opinion, of the greatest accuracy in working. I think this explanation will suffice for the reconciliation of my two statements.

As already stated, I have objected to a new name being given to an instrument identical with the one invented and named by myself, except that the readings are taken in a new way; but since then I have met with another reason why the name "gravitolumeter" should not be applied to the instrument. That name was bestowed years ago by Houzeau on another instrument of totally different principles and use (*Compt. Rend.*, lxxxvii., 747; and xc., 870), and it would be likely to cause great confusion if designations previously proposed for totally different instruments were applied to new ones.

Professor Japp further says: "The acknowledgments of obligation throughout my entire note could hardly have been more profuse." But he seems to have overlooked the following passage at the end of my first paper in the *Berichte* in which: "*I reserve to myself the further extension of the principle embodied by my gas volumeter*, in this and in other directions, as well as the improvement in detail of the instruments shown here only in outline; but *I shall be grateful for any suggestions on the part of other scientists.*" In the *Zeitschrift für Angewandte Chemie*, 1890, 142, more than a year before Professor Japp's first note, I repeated the above, adding that I intended to employ the name "gas volumeter."

Professor Japp admits that I have priority in the principle of reading off volumes of gases directly as weights, as when employing the gas volumeter for the estimation of nitrogen in organic combustions and for vapour densities. I had further claimed that I had attained the end of reading off volumes of gas directly as weights, by employing a certain weight of the substance to be analysed. To this Professor Japp objects that I do not find absolute weights, but merely percentage weights. Literally this is correct; but, as in almost all cases it is not the absolute but the percentage weights which are required, I fail to see the force of Professor Japp's objection.

I fully acknowledged the "sinnreiche Idee" of Professor Japp, which realises one of the "further extensions" of my principle foreshadowed in the above-mentioned

passage of my first paper; but I venture to submit, firstly, that it was not called for except in a limited number of cases; secondly, that it involved a loss of accuracy in the reducing operation. Both of these assertions I must maintain.

As for the first, I had already provided for all ordinary cases. In gas analysis proper, the reduction of volumes to weights is only quite exceptionally called for; in the gas-volumetric analysis of solid or liquid substances, the direct estimation of the percentage weight by my method is a distinct advantage over that of the absolute weights as shown above; and for the estimation of nitrogen and vapour densities it is necessary to employ, in lieu of gas burettes, specially constructed instruments, as described in my former papers.

According to my second criticism, Professor Japp's special form of regulator admits of only $\frac{1}{2}$ th (perhaps even $\frac{1}{4}$ th) of the accuracy yielded by the form which I prefer. This he tries to refute by taxing me with ignorance of "a commonplace of physical measurement," namely, that there is no advantage in making one of the inter-dependent parts of a determination much more accurate than another; but he is in error, for he assumes that I generally work with a 50 c.c. gas burette, whilst, as a matter of fact, I prefer, wherever possible, to work with far greater volumes, for which purpose the gas burettes, as shown in my various papers, are constructed to hold up to 150 c.c. An uncertainty of $\frac{1}{20}$ th in 100 with the large gas burette is exactly the same as in my regulator, namely, $\frac{1}{2000}$ th, as against $\frac{1}{500}$ th, the probable error with Professor Japp's regulator, "calculated on the basis of 25 c.c. as the average amount of gas measured." By means of a small movable straight edge, combined with a spirit level (the description of which I shall shortly publish), I can attain such accuracy in levelling the mercury in both tubes that the above minimum of error is actually realised. Even with 50 c.c. of gas in the burette, the accuracy is—

$$\frac{1}{50 \times 20} = \frac{1}{1000} \text{th.}$$

This is, I think, sufficient refutation of Professor Japp's charge of ignoring "a commonplace of physical measurement."

I will lastly explain a passage in my note in the *Berichte* which Professor Japp seems to have misunderstood, the fault being doubtless attributable to the extreme conciseness of that note. I there said that by employing a volume of 25 c.c. only, in the regulator, the accuracy of reading is *a priori* reduced to $\frac{1}{2}$ th, and, on account of the inconvenient form of the tube, probably even to $\frac{1}{4}$ th. The "inconvenient form" is that of a cylinder of equal width throughout as compared with that of an instrument bulged out at the top, in which only the bottom part is cylindrical and graduated, and the divisions may therefore be much larger than in the former case. In England, the bottom part need only hold 10 or 15 c.c.; at Zurich or Munich, 20 c.c. A 50 c.c. burette would have to be made very inconveniently long, if equally large divisions (easily readable to $\frac{1}{40}$ th) had to be provided.

*78. "The Composition of Cooked Vegetables." By Miss K. J. WILLIAMS.

The vegetables examined after cooking were:—Artichoke (Jerusalem), broad bean, haricot bean, beetroot, cabbage, carrot, cauliflower, celery, cucumber, lettuce, mushroom, onion (Spanish), parsnip, pea (green), potato, radish, salsify, scarlet runner, sea-kale, spinach, tomato, turnip, and vegetable marrow.

Determinations were made in these of the following:—

Water.
Carbon and hydrogen.
Nitrogen (total) by Dumas method.
Nitrogen by soda-lime combustion.
Nitrate extracted by dilute alcohol.
Ashes.
Sulphur.

Woody fibre by digestion with dilute sulphuric acid, &c.

Cellulose by Schulze's potassium chlorate method.

Carbohydrate convertible into glucose.

Fat.

Heat of combustion.

The results are given in a series of tables.

DISCUSSION.

Mr. WARINGTON remarked that the determinations of the heat of combustion were of considerable value, as these were the only data on which, at present, a comparison of the relative values of the different foods could be based; to which Dr. ARMSTRONG objected that the value of a vegetable food must depend both on the amounts of carbohydrates and albumenoids present and on their character, and therefore it did not seem probable that the determination of the heat of combustion would be of such special value. Mr. WARINGTON then pointed out that the quantity of albumenoids required for the renovation of tissue in the human body was so small (at most 40 grms. per day) that it could hardly fail to be present in an ordinary mixed diet; unless, therefore, an increase were being made to the nitrogenous tissues, the value of a food practically depended upon the amount of heat which it could generate in the body, a remark which the Chairman subsequently said his experience of vegetarian diet enabled him to corroborate.

Dr. KIPPING asked whether any attempt had been made to determine the effect on their composition of alterations in the mode of cooking vegetable foods.

Professor RAMSAY, who had given an account of the paper, said in reply, that in his opinion more value would attach to the determinations of heats of combustion if the digestibility of the foods had also been ascertained. As to the influence of modes of cooking, considerable differences had been noticed by Miss Williams between potato boiled in the skin and without skin, but this was the only case hitherto studied.

*79. "Metallic Hydrosulphides." By S. E. LINDER and HAROLD PICTON.

The authors have investigated the sulphides of copper, mercury, arsenic, antimony, cadmium, zinc, bismuth, silver, indium, and gold (*cf. Proc. C. S.*, 1890). With the single exception of bismuth, all these metals form hydrosulphides of a more or less complicated character, which, in most cases, undergo molecular condensation with elimination of sulphuretted hydrogen when submitted to the action of acids. Taking copper as a type, on treatment with sulphuretted hydrogen, copper hydrate forms a solution of the hydrosulphide $7\text{CuS}_2\cdot\text{H}_2\text{S}$. Acetic acid, in presence of excess of sulphuretted hydrogen, promotes molecular condensation, a product being formed which has approximately the composition $9\text{CuS}_2\cdot\text{H}_2\text{S}$; while acetic acid, in absence of sulphuretted hydrogen, promotes the formation of a product approximately represented by the formula $22\text{CuS}_2\cdot\text{H}_2\text{S}$. Chlorhydric acid produces still further condensation. Mercuric sulphide forms products approximately represented by the formulæ $31\text{HgS}_2\cdot\text{H}_2\text{S}$; $62\text{HgS}_2\cdot\text{H}_2\text{S}$. The latter formula represents the precipitate formed in presence of acid, and is a remarkably stable substance. Zinc sulphide solution obtained from the hydrate contains about 14 per cent excess of sulphur as sulphuretted hydrogen; in presence of acetic acid, a product represented approximately by the formula $12\text{ZnS}_2\cdot\text{H}_2\text{S}$ is formed.

The authors regard their results as evidence tending to support the conclusions that the metallic sulphides are in most cases polymerides of very high molecular weight.

*80. "The Physical Constitution of some Sulphide Solutions." By HAROLD PICTON.

The author has specially examined the solutions of mercuric, antimonious, and arsenious sulphides. In each case the whole of the dissolved sulphide is found to be present in the form of very finely divided particles.

Arsenious sulphide is found capable of existing in "solution" in three distinct types of sub-division. The following examples illustrate the main characteristics of sulphide "solutions":—

Mercuric Sulphide.—Particles are visible under the microscope (1000 diameters); is not diffusible even in absence of a membrane.

Arsenious Sulphide (α).—Particles are just visible.

Antimonious Sulphide.—Particles are not visible and it is not diffusible, but particles are detected by their power of scattering light, the scattered light being polarised.

Arsenious Sulphide (β).—Not diffusible; the particles scatter and polarise light.

Arsenious Sulphide (γ).—Diffusible in the absence of a membrane; particles are shown to exist by optical behaviour.

The solutions examined exhibit a series passing from those in which the particles of the solid are visible to those in which the particles simulate the phenomena of liquid diffusion, and, although not visible to the eye, are detected by their power of scattering light.

*81. "Solution and Pseudo-solution." Part I. By HAROLD PICTON and S. E. LINDER.

The authors advance what they regard as a good *prima facie* case for the belief that there is a continuous series of grades of solution passing without break from suspension to crystallisable solution. They hold that in the lowest grades of solution a certain loose attraction exists between the particles and the molecules of the solvent. This conclusion they support with experimental evidence gathered from their own work and from other sources. They regard the very finely divided particles in the lower grades of solution (colloid solution) as large molecular aggregates retaining many of their molecular properties. They consider that in passing up through the different grades of solution, these aggregates on the whole become smaller and the forces by which they are held in solution become more definitely those of chemical attraction. They describe a new property, which seems to hold for a large range of solutions, extending from suspension to crystallisable solution. This property consists in the repulsion of the dissolved substance, as a whole, from one of the electrodes of a battery immersed in the solution. Thus, in the case of colloidal arsenic sulphide, the sulphide aggregates are repelled from the negative electrode. They are also repelled, but much less strongly, from the positive electrode. In the case of the crystallisable colouring matter, Magdala red, in absolute alcohol, an exactly similar phenomenon is observed, but the repulsion is this time from the positive electrode, and there is no perceptible repulsion from the negative electrode at all. The property is of much interest in itself, but also as exhibiting similarities between the different grades of solution.

DISCUSSION.

Mr. PAGE suggested that observations on the nature of solutions, such as those described by the authors, might with great facility be carried out in capillary tubes under the microscope.

Mr. WALLEN said that in working with electro-coppering solutions containing resin in suspension, he had had occasion to notice a clearing of the liquid at the anode, such as had been referred to.

Professor RAMSAY said that the problem of Brownian motion, or pedesis, had engaged his attention since 1878, when he published a paper in the *Proceedings of the Geological Society* bearing on the settling of mud in salt water. The problem attacked by Messrs. Linder and Picton was one in which he thought pedesis played an all-important part, as the small particles, the existence of which had been proved by their power of polarising light, were in exceedingly rapid motion. Messrs. Linder and Picton had shown that there is a regular transition from visible particles to particles or molecules such as those of oxyhæmoglobin. It must, therefore, be concluded that such exceedingly small particles are also in rapid motion;

and the smaller the particles, the more rapid the motion. Pedesis had not received, as yet, any satisfactory explanation; the only fact which appeared to throw any light on its nature was that the addition of a salt to the solvent, rendering it an electrolyte, hindered pedesis, and finally caused coagulation and settling. The discovery of the true nature of pedesis would in all probability be the key to the problem of the nature of solution.

Mr. WARINGTON pointed out that the coagulation of clay by salts had been studied by Schloesing (*Chimie Agricole*, p. 62; Frey's "Encyclopédie," tome x; and W. Skey. CHEM. NEWS).

Mr. HERBERT JACKSON said that the phenomena discovered by the authors were similar to those observed in the case of the liquids produced during the washing of many precipitates, such, for instance, as lead hydrate or silver nitroprusside, which refuse to settle completely as soon as the liquid in which they are diffused becomes approximately pure water, or which show a tendency to come through the paper when washed on a filter. Such precipitates can be made to furnish turbid liquids in which the particles are so fine that they will not settle for many months, although, as is well known, the addition of a drop or two of a saline solution, e.g., sodium acetate or potassium nitrate, will cause rapid deposition of the solid.

These opalescent liquids give the results described and shown by the authors when examined at right angles to a narrow beam of strong light.

He had found in the case of lead hydrate that the microscope revealed moving particles with an average diameter of $1/35,000$ of an inch. Some, in the case of silver nitroprusside, were less than the $1/100,000$ of an inch. The limit of separation with lenses and illuminators giving the greatest possible angle for water immersion (viz., $\times 33$ numerical aperture) is:—

For λ 5269	128,225 lines to the inch.
„ λ 4861	138,989 „ „
„ λ 4000	168,907 „ „

In the case of particles separated from one another by considerable intervals, these limits will be exceeded, as the dark diffraction outlines will give an apparent measurement of the particles distinctly greater than they really are; but it is quite clear that it is impossible to call a liquid homogeneous because the microscope fails to show structure.

All that can be said is that the particles in water, if not visible with lenses of the greatest possible angle for water, are probably not much greater than the $1/180,000$ of an inch in diameter. Of course, it must be understood that changes in the limits will be observed when the refractive index of the particles differs very greatly from that of the fluid in which they are diffused, as is the case with As_2S_3 in water. It seems probable, therefore, that the phenomena observed in the cases of As_2S_3 and others which were mentioned, differ only in degree, and not in kind, from those in the cases of Sb_2S_3 and similar bodies, and from the opalescent liquids obtained in washing many precipitates.

*82. "The Change Proceeding in an Acidified Solution of Sodium Thiosulphate when the Products are Retained within the System." By A. COLEFAX, B.A., Ph.D.

Experiments were carried out in the following manner:—A certain volume of a solution of sodium thiosulphate, acidified with an equivalent quantity of acid, was enclosed in a small glass bulb, from which the air had been displaced by carbon dioxide; several such bulbs were filled and placed in a bath at a fixed temperature, and at certain definite times after acidification the contents of a bulb was titrated by means of an iodine solution. The initial titration of the acidified sodium thiosulphate at the moment of acidification being known, the extent of chemical change is given by the iodine titration. The sulphurous acid resulting from the decomposition of thio-

sulphuric acid possesses a titration in terms of iodine the double of that of the undecomposed thiosulphuric acid. The possible sources of error are considered under the heads "Oxidation of sulphurous acid," "Titration complications," and "Incomplete saline decomposition." A further check is afforded by the determination of the acidity of the solution after the iodine titration is made. For a solution of sulphurous acid there is a constant ratio between the iodine titration and the acidity of the solution after the iodine titration has been made. This value was determined for the particular iodine and ammonia solutions by means of a pure solution of sulphurous acid. Hence, whether or not the whole of the increase in iodine titration in the acidified solution of sodium thiosulphate is due to sulphurous acid can be ascertained by a determination of the two values, iodine titration and acidity developed after titration with iodine.

The author concludes that the change proceeding in an acidified solution of sodium thiosulphate when the products, viz., sulphurous acid and sulphur, are retained in the system, is a reversible one: a limit being reached a certain time from the time of acidification. The value of this limit is affected by (1) state of concentration, (2) ratio of the mass of acid relative to the sodium thiosulphate, (3) the nature of the acidifying acid, (4) the temperature. Sulphurous acid cannot prevent the decomposition of thiosulphuric acid. The presence of both products of the change in the system seems essential for the attainment of a limit value; for sulphurous acid, when initially present in the system at the time of acidification, has but a small effect upon the values expressing the extent of chemical change. A higher temperature favours the interaction of sulphurous acid and hydrogen or sodium thiosulphate, a secondary change which proceeds at lower temperatures with extreme slowness.

Spring's statement that sodium trithionate is formed by the interaction of iodine, sodium sulphite, and sodium thiosulphate, seems to be wrong; the author finds that in adding to a solution of iodine a mixed solution of sodium thiosulphate and sulphite, no sodium trithionate is produced; the sodium sulphite is completely oxidised to sodium sulphate.

*83. "The Action of Sulphurous Acid on Flowers of Sulphur." By A. COLEFAX, B.A., Ph.D.

Debus's statement that sulphurous acid has practically no action on sulphur is not confirmed. Sulphurous acid acts on flowers of sulphur at the ordinary temperature of the air, and produces thiosulphuric acid and a polythionic acid, probably trithionic acid. No pentathionic acid was found. According to Flückiger (*Fahresbericht*, 1853, p. 149), sulphurous acid gave, by its action on flowers of sulphur, thiosulphuric acid. The presence of a polythionic acid is proved by a comparison of the iodine titrations, and the acidity titrations before and after the addition of iodine requisite for the iodine titration. It is thus shown that there is present a considerable quantity of an acid having no iodine titration, and which is not merely oxidised sulphurous acid. Qualitative tests point to the presence of thiosulphuric acid, or trithionic acid, or a mixture of the two. Not even in the dark is sulphurous acid without action on sulphur. A higher temperature (say 80–90° C.) favours the action of sulphurous acid on sulphur; water has no action on flowers of sulphur, either at ordinary temperatures or at this higher temperature.

84. "The α - and β -Modifications of Chlorobenzene Hexachloride." By F. E. MATTHEWS, Ph.D.

By the action of chlorine on chlorobenzene in presence of a dilute solution of sodium hydroxide, the author obtains a mixture of α - and β -chlorobenzene hexachloride, together with oily products which have not been investigated (*cf. Proc. Chem. Soc.*, 1890). The solid portion can be separated from the oily substances only with difficulty by pressure between filter-paper and washing with light petroleum. The α - and β -compounds are separated by means of steam distillation, the β -compound being much

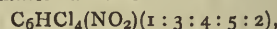
less readily volatile, and subsequent re-crystallisation from alcohol, benzene, or light petroleum.

α -C₆H₅Cl₇ is a colourless, crystalline substance, closely resembling α -benzene hexachloride in its properties; it melts at about 146°, and can be sublimed if carefully heated, but if heated too strongly, or on warming with an alcoholic solution of potassium hydroxide, it is quantitatively resolved into 1:3:4:5-tetrachlorobenzene and hydrogen chloride; on boiling an alcoholic solution with zinc-dust, chlorobenzene is obtained.

β -C₆H₅Cl₇ is only obtained in small quantity; it is more stable than the α -compound, and melts at about 260°; it is decomposed on heating either alone or with alcoholic potash, yielding the same tetrachlorobenzene as the α -substance.

Meunier's method of separating α from β -C₆H₅Cl₆ by means of an alcoholic solution of potassium cyanide has been investigated, and has been found to depend on the conversion of the α -C₆H₅Cl₆ into 1:2:4-C₆H₃Cl₃, the cyanide playing the part of a weak alkali.

1:3:4:5-C₆H₂Cl₄ has been investigated, with the result that the author is of opinion that the melting-point 50–51°, assigned by Beilstein and Kurbatow, is correct, and that Otto and Ladenburg, and Jungfleisch, who all give the melting-point considerably lower, were dealing with impure material. The nitro-derivative,—



was prepared and found to melt at 23° (Beilstein and Kurbatow, 21–22°).

The action of bromine on benzene in the presence of alkali has also been studied, and is found to yield C₆H₄Br₂, the product being the same whether gaseous or liquid bromine was used. On mixing monochlorobenzene with bromine under water and allowing the mixture to stand for about a week, a considerable amount of pure chlorobromobenzene was obtained.

The author calls attention to a paper by Sachse (*Ber.*, xxiii., 1363), in which Sachse shows that there are two positions of stability of the hexamethylene ring. According to Sachse's hypothesis, there should be two substances of the formula C₆H₆Cl₆ capable of existence, but three substances of the formula C₆H₅Cl₇, of which the two α -modifications would probably have very similar properties.

(To be continued.)

NOTICES OF BOOKS.

Methods of Gas-Analysis. By Dr. WALTHER HEMPEL, Professor of Chemistry in the Dresden Polytechnicum. Translated from the Second German Edition by L. M. DENNIS, Assistant Professor of Analytical Chemistry in Cornell University. Small 8vo., pp. 384. London and New York: Macmillan and Co.

If we pronounce this work not merely good and useful, but even admirable, we shall not be guilty of exaggeration. There can be in these days no need to enlarge on the importance of gas-analysis whether for purely scientific or for technical work. English-speaking chemists will therefore, doubtless, gladly welcome the appearance of a version of this special manual prepared by so competent and experienced an authority as Dr. Hempel. The general principles of the art, the methods to be employed in working upon different substances, and the special precautions to be observed are given fully and clearly. The illustrations, 101 in number, are well drawn, and are selected so as to make the instruments and the operations fully intelligible.

The work consists of three parts, each divided into several chapters. The first part treats of general methods, such as the collecting and keeping of gases, the apparatus for technical gas-analysis, and that for exact gas-analysis

the arrangement and fittings of the laboratory, in which every precaution is duly explained. The second part embraces special methods. A comparison is given between the results of an exact analysis made over mercury and two partial analyses executed over water. The differences appear decidedly smaller than it might have been expected. Particular attention is given—as is quite justifiable—to the detection and determination of carbon monoxide. The most delicate method, however, is out of the reach of English chemists, as in it mice are employed. Hence the process would be denounced as “vivisection,” and would subject the operator to severe penalties.

The author calls in question the assertion of Vogel and of Wolffhügel that proportions of carbon monoxide smaller than 0.25 per cent may be disregarded from a sanitary point of view. Decided symptoms of poisoning are produced in mice if 0.05 per cent of carbon monoxide are inhaled. He contends—and we unreservedly support his view—that the presence of any carbon monoxide should be regarded as inadmissible, so that heating appliances which allow it to mingle with the air of dwelling-rooms, workshops, &c., are to be condemned.

Instructions are given for the examination of gun-cotton and nitroglycerin in a vacuum,—a very welcome improvement, as accurate analyses of these substances can rarely be obtained at the ordinary pressure of the atmosphere.

The determination of the heating-power of fuel is a subject which does not often figure in manuals of gas-analysis.

the Journal just mentioned, it would appear that in that gentleman's hands the nitric oxide process does not work at all. His results vary from 77.5 to 122.5 per cent of the amount of oxygen operated upon, and the difference between the process in our hands and in his is this: whilst he shows this wide variation, we show a variation of less than 1 per cent of the oxygen operated upon. In Koninck's paper he says that “the *modus operandi* was practically identical with that employed by Wanklyn and Cooper,” and then proceeds to say explicitly what he really did.

In making the assertion that his *modus operandi* was practically the same as ours, Koninck has done himself an injustice. Cooper and myself do not claim for ourselves such superior manipulative skill that a *modus operandi* which in Koninck's hands is 25 per cent above or below the truth becomes less than 1 per cent distant from the truth in our hands. The difference is not so much in the skill of the operators as in the *modus operandi* itself.

In order that the reader may be in a position to judge of the importance of the differences between our *modus operandi* and that followed by Koninck, I will quote a passage from the preface to our “Air Analysis.”

“The accuracy of modern technical processes of gas analysis has, we are aware, often been called in question. In particular it has often been said that measurements over water cannot be accurate because of the solubility of all gases in water. If in the Hempel apparatus the large bulk of liquid were boiled out so as to be devoid of air, there might be reason for the objection; but it is not, and therefore the error is restricted to that which arises from the difference of solubility of different gases. It is further to be noted that this error is eluded to a great extent, inasmuch as the contact between the gas and the liquids in Hempel's apparatus is too superficial to bring out these differences of solubility. In order to introduce serious solubility error, shaking up might be resorted to, and in that manner possibly some error might arise.”

In Koninck's experiments the solubility error comes in in its worst and most exaggerated form; in our experiments the solubility error is avoided.

We welcome Koninck's paper as a warning to the readers of our book, who must not expect to succeed unless they follow our directions implicitly.—I am, &c.,

J. ALFRED WANKLYN.

Laboratory, New Malden,
Surrey.

CORRESPONDENCE.

ESTIMATION OF FREE OXYGEN BY MEANS OF NITRIC OXIDE.

To the Editor of the Chemical News.

SIR,—It is matter of history that about a hundred years ago free oxygen was estimated by means of nitric oxide, and that by that method Priestley obtained results which were inaccurate and variable, whilst Cavendish obtained almost absolutely the same figures for the oxygen of the air as Bunsen and more modern observers who have employed the method of explosion in presence of excess of hydrogen gas. The question thence arose: How came it to pass that Cavendish could get correct results whilst other experimenters, operating by the same method and at the same date, obtained discordant and erroneous results?

As readers of the CHEMICAL NEWS who may have chanced to read our former communications will be aware, my colleague Mr. Cooper and myself have answered the question thus:—Under proper conditions—which admit of easy statement—the nitric oxide method answers perfectly, but when the proper conditions are not complied with, the method fails.

And in our little book entitled “Air Analysis” we have given very explicit directions for the performance of the analysis in question. From our publishers we learn that many hundred copies of our book are now in the hands of the public, and doubtless by this time we have a little army of experimenters who are ready to do battle for the honour of those fine old English chemists to whom we owe one of the easiest, most beautiful, and most accurate analytical processes in the whole range of chemical analysis.

Such being the case I am much amused by an attack upon us by L. L. De Koninck in the January number of the *Journ. Chem. Soc.*, of London (*vide p. 97*).

From Koninck's paper, as will be seen on reference to

METHYLATED SPIRIT.

To the Editor of the Chemical News.

SIR,—As regards obtaining unmineralised methylated spirit, it is less roundabout to make direct application to the Commissioners of Inland Revenue, Somerset House, London.

They, on receiving the application, will see that the proper officer deals with the matter. Your correspondent spoke of a £200 bond, but the Board of Inland Revenue do not, we are given to understand by Excise authorities, contemplate demanding this where less than 50 gals. is required per annum.

Our experience hitherto is that no one connected with a medical or scientific institution has been refused the power of obtaining unmineralised methylated spirit, provided that the element of retailing does not come in, and that he be able to order not less than five gallons at a time of a methylator, not a retailer.—We are, &c.,

A. and J. WARREN,

Wholesale Druggists and
Licensed Makers of
Methylated Spirit and Finish.

23 and 24, Redcliff Street, Bristol,
January, 20, 1892.

THE DENSITIES OF SULPHURIC ACID.

To the Editor of the Chemical News.

SIR,—It is with regret that I find that any words of mine in your columns should have been considered by Prof. Lunge to be stronger than the circumstances of the case warranted, and I should have been pleased to apologise to him if he had traced his mistakes to any carelessness or ambiguity on my part. There is certainly much excuse for irritation when one finds a critic condemning a most laborious piece of work on the grounds that the very thing had been done which one had taken the greatest pains to point out to readers had *not* been done.

Prof. Lunge denied the accuracy of my determinations as far as their use in constructing a table was concerned by stating that I maintained the *actual* strength of the acid to be known to 0.001 per cent, and that I had obtained this result by analysis. The fact was, that I stated the strength to be known to 0.01 per cent, and that this result was *not* obtained by analysis. In excuse he now pleads that I gave the *relative* accuracy of the strength of the various solutions as 0.0001 per cent,—a value which, however, does *not* agree any better than 0.01 with his 0.001 per cent, and which, even if it did, could not be confounded with the *actual* accuracy,—and that in those tables which I used for the purposes of examining the results, I printed the strengths as given by analysis, stating, however, most clearly that these strengths were “ $\frac{712}{1,000,000}$ too low.”*

But what was or was not quoted in these tables is not to the point, for Prof. Lunge's remarks applied solely to the table of calculated values, and now that I have shown him that for the construction of this table the results of the analyses were *not* taken, and that neither the analyses nor the method used for determining the actual strengths were represented as giving the percentages correct to the “impossible” nicety of 0.001, and have thus removed the *only* objection which he raised against my work, he ought in “common fairness” (to use his own expression) to withdraw his opposition. It certainly appears strange to me that after I have now for the fourth or fifth time pointed out that the percentage values which I quoted had a relative accuracy of 0.0001 and an actual accuracy of 0.01, that Prof. Lunge should represent me (bottom of p. 13) as claiming “for them only a *relative* accuracy.”

But Prof. Lunge seems fated to misrepresent me, for even in his communication to your journal he states that the method adopted by me for ascertaining the strength of the acid was “founded upon the hypothetical basis that the pure (acid) must have the lowest freezing-point.” This would, indeed, be an hypothetical basis! What my method was founded on was that a pure substance has a *higher* freezing-point than an impure one, and this statement is based, not upon hypothesis, but upon fact. Out of the many thousands of cases which have been investigated there are only one or two in which the addition of impurity has been found to raise the freezing-point of a liquid, and the nature of the results with sulphuric acid can leave no doubt but that this substance does not form another instance of such abnormal behaviour.

I may add that Prof. Lunge's conjecture that Mr. Richmond made the same mistake as he did, and neglected my notification that the percentages given in my Tables I. to VI. were $\frac{712}{1,000,000}$ too low, is in direct contradiction to Mr. Richmond's statement that the values deduced by him agreed exactly with those given by me in Table VII., where the percentages are not $\frac{712}{1,000,000}$ too low.—I am, &c.,

SPENCER PICKERING.

Harpenden, Jan. 9, 1891.

* In the paragraph which Prof. Lunge quotes in the CHEM. NEWS, vol. lxx., p. 13, he omits the sentence which comes after the word “mentioned”; it is, “in all the other cases” (i.e., the cases in which the strengths quoted depended on analysis) the percentages quoted are $\frac{712}{1,000,000}$ too low,” a sentence which renders his conclusion that I accepted the analysis as giving the true strength of the acid entirely untenable.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 1, January 4, 1892.

The past year has brought many changes in the Academy. Among the members Edmond Becquerel, M. Cahours, and Alfred Richet are dead. Of its foreign associates the Academy has lost the ex-Emperor of Brazil, and of its correspondents MM. Kronecker, Boileau, Ibañez de Ibero (Marquis de Mulhacen), Weber, Stas, De Andrade Corvo, and Palasciano. Seven vacancies remain to be filled.

Remarks on the Mechanism of the Fixation of Nitrogen by Soil and Plants with reference to the Reply of MM. Schloesing, jun., and Laurent.—Arm. Gautier and R. Drouin.—A brief controversial note.

Direct Combination of Nitrogen with the Alkaline Earthy Metals.—M. Maquenne.—Hitherto we have only known a small number of metals capable of directly fixing nitrogen in notable proportions, and those which, like magnesium and aluminium, form definite nitrogenous compounds, manifest this property only at white redness. The author finds that the alkaline earthy metals give rise to the same reaction at a cherry-red heat, forming nitrides which are immediately decomposable by water with production of ammonia. The author's process consisted in heating a rich amalgam of the metal studied (15–20 per cent), in an atmosphere of pure dry nitrogen. The experiment must be made in a boat of iron or nickel as platinum is rapidly attacked. The temperature is kept at dull redness for half an hour so as to expel the greater part of the mercury. It is then raised for a few instants to bright redness and let cool. The nitride appears as a brown mass of a semi-metallic lustre, very easily attacked by moist air. The experiment succeeds most readily with barium. If the nitride is brought in contact with water hydrogen is evolved whilst ammonia remains in solution. The result is obtained in the entire absence of carbon.

Nitration of the Hydrocarbons of the Methane Series.—M. Konovaloff.—The normal hydrocarbons of the methane series may be nitrised by the action of weak nitric acid, and yield secondary nitro-products as principal products. Secondary nitro-hexane and nitro-heptane yield by the action of nitrous acid a colouration indicating the probable formation of pseudonitrole. On the reduction of these nitro-products we obtain corresponding amines and ketones.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Medical, 8.30.

Society of Arts, 8. “Developments of Electrical Distribution,” by Prof. George Forbes, F.R.S.

TUESDAY, 26th.—Royal Institution, 3. “The Brain,” by Prof. Victor Horsley, F.R.S.

Society of Arts, 8. “The Woodcuts of Gothic Books,” by William Morris, M.A.

Royal Medical and Chirurgical, 8.30.

Institute of Civil Engineers, 8.

Photographic, 8.

WEDNESDAY, 27th.—Society of Arts, 8. “The Scientific Value of Lovibond's Tintometer,” by F. W. Edridge-Green.

THURSDAY, 28th.—Royal, 4.30.

Royal Society Club, 6.30.

Institute of Electrical Engineers, 8.

Royal Institution, 3. “Some Aspects of Greek Sculpture in Relief,” by A. S. Murray.

FRIDAY, 29th.—Royal Institution, 9. “Tales of the Scottish Peasantry,” by Sir George Douglas, Bart., M.A.

SATURDAY, 30th.—Royal Institution, 3. “The Induction Coil and Alternate Current Transformer,” by Professor J. A. Fleming, M.A., D.Sc.

ERRATUM.—P. 27, col. 2, line 3, for “Brown” read “Blown.”

THE CHEMICAL NEWS.

VOL. LXV., No. 1679.

NOTES FROM FLORIDA ON THE GLASER METHOD FOR THE DETERMINATION OF IRON AND ALUMINA.

By BEVINGTON H. GIBBINS, F.C.S., Ocala, Fl.

It is a curious fact that in all the literature bearing on the Glaser method for the determination of iron and alumina oxides, which has been published in the past year or two, no further reference has been made to the suggestion of Messrs. Teschemacher and Smith in the *CHEMICAL NEWS*, vol. lxiii., p. 84. The addition of ammonia to the alcoholic acid solution of the phosphates is there recommended previously to the expulsion of the alcohol. The writer adopted this course of procedure at the time of its publication, and has never found it otherwise than satisfactory when certain precautions are observed.

It is, of course, obvious that if a large excess of ammonia is here added, magnesia, if present, will most certainly be deposited as magnesium ammonium phosphate. That this is not the case when ammonia is added carefully with only a drop or two in excess, any operator can easily prove for himself by adding a large excess of magnesium oxide to a sample of phosphate of known composition. On putting such a mixture through the Glaser process, a precipitate of phosphates of iron and alumina is obtained in due ratio to that in the original phosphate, which can easily be proved to be free from magnesia. The writer has obtained this result when 25 per cent of magnesia was added.

Daily experience for over a year has shown that the simplest and cleanest way to conduct the operation is to place the aliquot portion of the alcoholic acid solution in a porcelain dish, and then to add ammonia of specific gravity 0.96 from a burette, with constant stirring. Testing with a strip of litmus paper answers well. If the ammonia is too strong, a partial separation of the alcohol takes place, rendering it difficult to hit the point of neutrality. When neutral the dish is placed on a steam bath, and in about three quarters of an hour the alcohol has usually disappeared. It is essential not to carry this evaporation to dryness, as, if the silica has not been completely eliminated previously, it will here be rendered insoluble. The contents of the dish are then washed out into a beaker, a few drops more ammonia added, and boiled thoroughly. Then, if it is cooled rapidly by placing the beaker in a pan of water, immediate subsidence ensues, and filtration may be proceeded with without delay.

I have found this method far more rapid than the evaporation of the alcohol from the acid solution, and the disagreeable results of the exposure of any organic matter to the action of sulphuric acid, and subsequent necessity for oxidation with bromine, are entirely avoided.

If ammonia of specific gravity 0.89 is added to the alcoholic acid solution, complete separation of the solution into two layers is noted, the alcohol being all contained in the upper layer, and the precipitate in the lower one. It was a question at one time in my laboratory whether the alcohol could not be thus eliminated by means of a separatory funnel, but in view of the fact that evaporation occupies less than an hour, and that other work can very conveniently be sandwiched in at this juncture, the idea was relinquished.

In some samples of Florida phosphates manganese is present to an appreciable extent. It is noticed in nearly all sample of the gravel which is found adjacent to the

deposits of "plate rock," and which is usually mixed with the "plate rock" in cargoes. In some instances I have picked out concretions of pyrolusite one-eighth of an inch in diameter, but it more often occurs in thin layers, and is with difficulty detached from the phosphate.

When manganese is present the precipitate of phosphates of iron and alumina will be found contaminated with it. In such cases, if the precipitate is, after partial washing, re-dissolved in dilute nitric acid, a little phosphate of ammonia added to the solution, and then ammonia until neutral, a second precipitate is obtained free from manganese. I should advocate this course in all samples of gravels and plate rock. I have never detected manganese in samples of boulder phosphate, nor in the pebble deposits of South Florida. The gravels referred to usually contain from 73—78 per cent of phosphate of lime, and can never be mistaken by anyone who has once seen them in the unground condition.

SEPARATION OF ARSENIC AND OF PHOSPHORIC ACID FROM MERCURY,

AS ALSO

DETERMINATION OF NITRIC ACID, CHLORINE, AND SODIUM, IN PRESENCE OF MERCURY AND PHOSPHORIC OR ARSENIC ACID.

AN INAUGURAL DISSERTATION.

By KONRAD HAACK.

For the separation of arsenic acid from mercury, present in the mercuric state, the substance is dissolved in a little hydrochloric acid, the solution is supersaturated with ammonia, and to the white precipitate thus formed there is added drop by drop a clear solution of potassium cyanide, not very dilute, until the white precipitate is completely re-dissolved. The solution is then first mixed with so much ammonia as amounts to one-fourth of the entire volume of the solution, and then with the same quantity of absolute alcohol. The arsenic acid is then precipitated in the ordinary manner, and in the filtrate which is slightly acidulated and diluted, the mercury is thrown down by sulphuretted hydrogen.

If the mercury is present in the mercurous state the substance is dissolved in a little nitric acid, a little hydrochloric acid is added, and a few particles of potassium chlorate, and the liquid is heated on the water-bath until it becomes clear and no longer smells of chlorine, proceeding afterwards as above.

Before applying this method of separation, the author had followed Rose's method, throwing down the mercury from the hydrochloric solution of the substance by means of phosphorous acid as mercurous chloride. The results, however, were never accurate, as the precipitation of the mercury was never complete even after standing for several days.

2. The separation of phosphoric acid from mercury is effected exactly in the same manner. The results are quite as accurate as by the sulphuretted hydrogen method.

3. The determination of nitric acid in presence of mercury and arsenic acid, or phosphoric acid, is founded upon the fact that a solution of barium hydroxide completely decomposes the metallic nitrates.

The solid substance is boiled for about fifteen minutes with a solution of pure barium hydroxide in excess. It is filtered whilst hot, and washed with hot water until baryta can no longer be detected in the washings. The filtrate contains the nitric acid as barium nitrate, and in addition barium hydroxide.

There is then passed into the filtrate a current of carbonic acid to remove the barium hydroxide until the alkaline reaction has disappeared. It is then boiled for half an hour to expel free carbonic acid, filtered whilst hot, and washed with hot water. The second filtrate, which contains merely barium nitrate, is largely diluted, and dilute sulphuric acid is added. From the weight of the barium sulphate precipitated the nitric acid present may be readily calculated.

If, in the substance containing the nitric acid, there is present beside mercury and arsenic—or nitric acid—an alkaline metal, the quantity of nitric acid present can be determined by this method only if the alkali present does not suffice to convert all the nitric acid into nitrate of alkali, and if the quantity of the alkali itself is already known. Only that part of the nitric acid is taken up by the baryta which the alkali does not suffice to combine with. The nitric acid united with the alkali cannot be determined but merely calculated.

4. For determining chlorine in presence of mercury and arsenic acid, or phosphoric acid, the solid substance is boiled for fifteen minutes with an excess of solution of baryta and filtered. The precipitate, after washing, contains no chlorine, and the filtrate no mercury. In the filtrate the chlorine is determined after acidulation with nitric acid in the usual manner as silver chloride.

5. For determining sodium in presence of mercury and phosphoric acid, the hydrochloric or nitric solution of the substance is mixed with baryta water until the reaction is slightly alkaline and then boiled for fifteen minutes. It is then filtered and washed until free from baryta. In the precipitate are found the mercury and the phosphoric acid, whilst the solution contains all the sodium, barium hydroxide, and barium salts.

After the baryta has been precipitated with sulphuric acid in the boiling solution previously acidified, and after the precipitate has been filtered off, the filtrate is first concentrated in a platinum capsule and then evaporated completely to dryness in a tared crucible. From the weight of the ignited residue, which consists of sodium sulphate, the proportion of sodium in the substance is known.

6. The determination of sodium along with mercury and arsenic acid is effected by heating the substance gently in a tared porcelain crucible along with solid ammonium chloride, until the weight is constant. The residue is taken as sodium chloride.

DETERMINATION OF PHOSPHORUS IN IRON AND STEEL.

By CH. MALOT.

THE phosphoric acid is first separated in the well-known manner as ammonium phosphomolybdate, the precipitate is dissolved in ammonia, and re-precipitated with magnesia mixture. After filtration the ammonium-magnesium phosphate is dissolved upon the filter in nitric acid of specific gravity 1.2, and the phosphoric acid is determined volumetrically with a solution of uranic nitrate. In this titration the author evades the spotting test with potassium ferrocyanide for detecting the end of the reaction by making use of tincture of cochineal, and of the property of uranium oxide to form a green lake with the colouring matter of cochineal. The nitric solution is mixed with a few drops of tincture of cochineal (obtained by treating cochineal with boiling water), an excess of the tincture being avoided, as a too intense colour interferes with the sensitiveness of the reaction. Ammonia is then added to the solution until a permanent violet colour is produced, and this colour is again removed by the addition of a drop or two drops of nitric acid.

He adds further 5 c.c. of a solution of sodium acetate (containing per litre 100 grms. of the salt), and then 50

c.c. of glacial acetic acid, heats to 100°, and titrates the hot solution with a neutralised solution of uranic nitrate of known efficacy. Each drop of this solution produces in the liquid mixed with cochineal tincture a greenish-blue spot the further the precipitation has advanced. It disappears on shaking, and the rose colour of the cochineal re-appears until the precipitation is complete.

As soon as all the phosphoric acid has been precipitated by the solution of uranic nitrate, the liquid takes a bluish-green colour, which is not affected by any further addition of uranic nitrate. If a drop of the solution is brought in contact with a particle of ferrocyanide there ensues no colouration; in order to produce a distinct brown colour a little more of the uranic nitrate solution must be added.

It is convenient to use a solution of uranium, of which 1 c.c. corresponds to 2 m.grms. phosphoric acid, and standardised to a solution of phosphoric acid of known strength, carefully observing the above conditions and heating the solution to 100°.

The results obtained by Malot, according to this method, always agree to $\frac{1}{10}$ c.c. or $\frac{1}{2}$ m.grm. phosphoric acid. As the method, in addition to its accuracy, is very expeditious, the author prefers it both to the "spotting" test with ferrocyanide and to the direct weighing of the magnesium pyrophosphate.—*Zeit. Anal. Chemie.*

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, January 9th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 166 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 166 samples examined, 160 were found to be clear, bright, and efficiently filtered. Four were recorded as "slightly turbid" (S.T.), and two as "very slightly turbid" (V.S.T.).

Although the generally turbid and flooded condition of the rivers throughout November was appreciably exceeded during the following month by reason of the heavy rainfall, the state of the December water supply showed upon the whole a distinct improvement. Thus, taking the Thames-derived supply for comparison, the mean degree of colour-tint was found to be reduced from 22.1 : 20 to 18.7 : 20; the mean amount of oxygen expended in oxidation from 0.101 grain per gallon to 0.079 grain; the mean

amount of organic carbon from 0.250 to 0.240 part in 100,000 parts; and the maximum amount of organic carbon in any single sample examined from 0.391 part to 0.319 part. Similarly, in the case of the New River and East London Companies' supplies for the two months respectively, the results obtained during December showed a similar improvement over those recorded in our previous month's report.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

ON A
RAPID METHOD FOR THE ACCURATE
RECOGNITION OF SULPHIDES, ARSENIDES,
ANTIMONIDES, AND DOUBLE COMPOUNDS
OF THESE BODIES WITH METALS.*

By CHARLES A. BURGHARDT, Ph.D., &c.

(Concluded from p. 44).

Antimony Sulphide.

Stibnite, Sb_2S_3 .—Fused in the same kind of apparatus as that used for the sulphides of arsenic, yielded sulphuric acid in the water and a mixture of Sb_2O_3 and Sb_2O_5 . A little sulphuric acid was also detected in the water which had been used to boil the residue in the fusion tube. On adding a solution of potassium bisulphate to the residue in the fusion tube, and a piece of pure metallic zinc, antimoniu-retted hydrogen was at once evolved, and a mirror of metallic antimony obtained on heating the delivery tube to redness. Other tests applied proved this mirror to be really antimony. The mineral did not give reactions for any other element likely to be present, hence it was sulphide of antimony.

If it is suspected that both arsenic and antimony are present in a mineral in large amount, they can be easily separated from each other by substituting sodium nitrate for ammonium nitrate, when a compound of antimony and sodium, insoluble in cold water, is obtained (antimoniate of sodium), whilst the arsenic forms arsenite and arsenate of sodium, both of which are soluble in cold water after standing some time.

Löllingite.

$FeAs_2$.—Fused with ammonium nitrate in a platinum crucible or porcelain crucible. Melt, red coloured. Dissolved in hot water gave the reactions for arsenious and arsenic acid with silver nitrate and the usual arsenic reactions. The insoluble residue gave the reactions for iron. The mineral was therefore an arsenide of iron.

Proustite.

Ag_3AsS_3 .—Fused in the same manner as the last-mentioned mineral, yielded a black residue containing arsenic oxide (this residue will be the subject of special examination, as it is peculiar). The melt was treated to separate the black residue. A solution of silver sulphate was obtained, which gave the characteristic reactions for silver and sulphuric acid. The black residue was treated with the acid potassium sulphate solution and metallic zinc, and arsenic was detected in the usual manner. The solution in water also gave the characteristic reaction for arsenic acid with silver nitrate. All the silver of the proustite was converted into sulphate, on account of the high percentage of sulphur in this mineral. The mineral was therefore a sulph-arsenite of silver.

Pyrrargyrite.

Ag_3SbS_3 .—Treated in the same way as the preceding mineral, sulphate of silver was obtained in solution in water, and insoluble antimonious and antimonie oxide (Sb_2O_3 and Sb_2O_5) remained as a residue. The antimony reactions were obtained, and only silver and sulphuric acid detected; consequently, the mineral was a silver sulph antimonite.

Argentite.

Ag_2S .—On treating this mineral in the same manner as pyrrargyrite, sulphate of silver was produced in small amount, owing to the small percentage of sulphur present in argentite. On adding a small quantity of "flowers of sulphur" to the powdered mineral, and then fusing the mixture with the ammonium nitrate, a larger quantity of silver sulphate was obtained. The solution gave the reactions for silver and sulphuric acid only; consequently, the mineral was a sulphide of silver.

Iron Pyrites.

Marcasite. *Pyrites*. FeS_2 .—Fused as above, gave a reddish brown residue of ferric oxide, Fe_2O_3 , and a brown solution in water, which gave the characteristic reaction for ferric salts with potassium ferrocyanide solution, and also the reaction for sulphuric acid. The mineral was therefore sulphide of iron.

Galena.

PbS .—Gave a white residue (insoluble in water) of lead sulphate, and nothing in solution. The residue was dissolved in hot hydrochloric acid, when a portion of the solution gave a white precipitate (of barium sulphate) on the addition of a solution of barium nitrate, and another portion of the hydrochloric acid solution, on being neutralised with sodium carbonate and boiled with a solution of potassium bichromate, gave the characteristic yellow lead chromate reaction. The white lead sulphate residue mentioned above, on being treated directly with the solution of potassium bichromate, also gave the lead chromate reaction. The mineral was therefore a sulphide of lead.

Copper-glance (Redruthite).

Cu_2S .—Gave a blue melt whilst hot, which became brown on cooling. The melt dissolved completely in water into a blue solution, which gave the usual reactions for copper and sulphuric acid. The mineral was therefore a sulphide of copper.

Bismuth-glance.

Bi_2S_3 .—The melt was brown when cold. A solution of sulphate of bismuth was obtained, which gave the reactions for bismuth and sulphuric acid. An excellent and delicate reaction for bismuth is that which was shown to me by Professor Bunsen, at Heidelberg, twenty-one years ago, which I have never yet seen described in any work on qualitative analysis. In applying it to the solution of the melt first add a slight excess of caustic soda solution to it, when a white precipitate of hydrated bismuthic oxide ($Bi_2O_3 \cdot H_2O$) is obtained. In another vessel add an excess of caustic soda solution to a solution of stannous chloride, when a white precipitate of hydrated stannous oxide ($Sn(OH)_2$) falls out, but immediately re-dissolves in the excess of caustic soda. The bismuth precipitate obtained as above is washed into a white basin and a portion of the caustic stannous solution poured upon it and well stirred with it, when very soon a dense black precipitate is seen in the white basin, this precipitate being an oxide of bismuth, Bi_2O_2 , formed by the reduction of the Bi_2O_3 through the SnO .

Millerite.

NiS with *Co* and *Fe*.—Gave a green solution of sulphate of nickel, which gave the characteristic reactions for nickel and sulphuric acid, and also those for cobalt and iron. There was an insoluble brown residue of ferric oxide from the melt. The mineral therefore was a sulphide of nickel.

* From the *Mineralogical Magazine*, Vol. ix., No. 43.

Copper Pyrites.

CuFeS₂.—Gave the same reactions as those obtained in the case of chalcocite with the addition of a copious reddish brown insoluble residue from the melt of ferric oxide. The solution of the melt in water was blue. The melt in the crucible was reddish brown. The mineral was therefore a sulphide of copper and iron.

Bourbonite.

CuPbSbS₃.—Melt after fusion yellowish green. Treated with water gave a solution of copper sulphate, in which both copper and sulphuric acid were detected as in chalcocite, &c. The insoluble residue (after dissolving out all the copper sulphate) was found to be sulphate of lead and antimonious and antimonie oxides. A portion of this insoluble residue was treated with acid sulphate of potassium (as in stibnite), when all the antimony was eliminated as antimoniuiretted hydrogen, and the residue of lead sulphate treated as the sulphate of lead obtained from galena, and the presence of lead demonstrated. The mineral therefore was a copper-lead sulph-antimonite.

Tetrahedrite, or Fahl ore.

Cu₈Sb₂S₇.—The melt was green whilst fusing, but brown when cold. Treated with water gave a blue solution of copper sulphate, ferric sulphate, and traces of zinc sulphate and arsenious acid. The usual tests were applied to this solution, and copper, iron, and sulphuric acid detected.

The residue insoluble in water was found to be antimonie oxide (*Sb₂O₃*) and ferric oxide. On boiling the residue with caustic potash, the *Sb₂O₃* was dissolved and the ferric oxide remained. On adding hydrochloric acid in excess to the antimonate of potassium and a piece of metallic zinc, antimoniuiretted hydrogen was detected in the way described above. The mineral therefore was a copper-iron, &c., sulph-antimonite.

Smaltite.

(*Co, Fe, Ni*) *As₂*.—The melt was pink whilst fusing. Treated with water and boiled, an insoluble residue of cobalt, iron, and nickel oxides remained, whilst arsenious acid passed into solution, and the arsenic was detected in the usual manner. The oxides of the metals thus obtained were dissolved in hydrochloric acid and tested chemically for cobalt and nickel, also iron, and these metals were detected.

Where arsenic and antimony combine with metals forming antimonides and arsenides, and no sulphur is present, oxides of the metals are obtained together with oxides of antimony and arsenic. By adding sulphur to these compounds, the metals are converted into sulphates and become soluble.

I have still to discover a good method for the separation and detection of cobalt and nickel, suitable for mineralogical analysis.

In conclusion, I must acknowledge the great assistance I have received from my assistant, Mr. Gilbert Rigg, in this investigation.

NOTE.—Since writing the above I have made some further experiments, and have succeeded in separating cobalt from nickel in the most complete manner. If the mineral is an arsenide or antimonide of cobalt and nickel it is fused as described in the treatment of smaltite, and when all the metals are converted into oxides a lump of ammonium nitrate is added to the melted mass from time to time, and the whole is kept gently simmering for three or four minutes. The melted mass assumes a pink colour due to the formation of nitrate of cobalt. After cooling, the melt is boiled out with water; NiO remains behind absolutely free from CoO. The cobalt nitrate solution is evaporated to dryness in a porcelain basin and ignited at about 250° C., when all the ammonium nitrate present is volatilised and pure pink cobalt nitrate remains in the

basin. If the mineral is a sulphide of nickel and cobalt, fuse it with 10 per cent of its weight of powdered carbon (previously added to the powdered mineral), and about four times its weight, or more, of caustic soda in a silver crucible. Sodium sulphide is produced, and dissolved out by water from the cooled melt, and the oxides of cobalt and nickel remain behind; they are then treated with ammonium nitrate as described above.—C. A. B.

THE OXIDATION OF METALLIC ARSENIDES
BY THE ELECTRIC CURRENT.*

By LEE K. FRANKEL.

THE decomposition of minerals and their subsequent oxidation by means of the electric current is a product of very recent origin. By reference to the literature of the subject, it will be found that the first attempt in this direction was made by Dr. Smith, in a paper published in the *Proceedings of the Chemical Section of the Franklin Institute*, vol. i., p. 52, in which the author has successfully completed the decomposition of chalcocopyrite, and gives the results of some preliminary investigation on chromite.

In a later and more exhaustive paper in the same journal, Dr. Smith has published his researches on the decomposition of other sulphides, and has proven conclusively that oxidation by the electric current gives results as quantitatively correct as those obtained by any wet or fusion method. In a still later paper by the same author (*Amer. Chem. Journ.*, vol. xiii., No. 6), experiments on various kinds of chromite indicate that the decomposition of this mineral is complete, if the conditions prescribed are closely followed. At present this completes the literature of the subject, and judging from the success so far obtained, it was deemed advisable to attempt the oxidation of the metallic arsenides, with the hope that the result would be similarly fruitful. These results and the methods used for obtaining them will be found appended below.

The apparatus used for this purpose was the same as that described by Dr. Smith in the *Proceedings of the Chemical Section of the Franklin Institute*, vol. ii., p. 53, and the method of using it was also substantially the same. The current generated from four storage cells of the Julien type was passed through the resistance frame, then through a Kohlrausch ampèremeter, and lastly up through the nickel crucible, the latter being in all cases the positive pole. As for the oxidations, the time required, the strength of current, &c., differed in each mineral respectively. For this reason no general plan can be prescribed, but the details of the work will be found for each mineral under its respective heading.

Gersdorffite (Ni.Fe.), As₂S.—The sample used for the decomposition came from Shladming. The method of procedure was as follows:—In a nickel crucible 1½ inches high and 1¾ inches wide, 25–30 grms. of solid caustic potash were placed. The contents of the crucible were heated until fusion took place, and the gersdorffite then carefully added. A current registering 1 ampère was passed through the mass for twenty minutes, the crucible being the anode. Towards the end of the operation the current was reversed for three minutes to remove any particles of mineral that might have been enclosed in the metal deposited on the cathode. After breaking the current the crucible was allowed to cool, then thoroughly disintegrated with water, and the resultant insoluble material (nickel and iron oxides) filtered off. The clear filtrate was acidulated with concentrated hydrochloric acid, and then made strongly alkaline with ammonium hydrate. The precipitate (silica and alumina from the

* Read at a meeting of the Chemical Section of the Franklin Institute, November 17, 1891.

caustic potash), which formed on the addition of the latter reagent, was filtered off, and magnesia solution added. The precipitate of magnesium ammonium arseniate which formed after standing twelve hours was filtered off, dissolved in dilute hydrochloric acid, re-precipitated with ammonium hydrate, filtered, dried, weighed, and ignited in a platinum crucible in the manner prescribed for this determination. The results obtained were as follows:—(1) 0.2777 grm. of ore gave 0.2853 grm. of magnesium pyroarsenate = 49.73 per cent arsenic; (2) 0.1137 grm. of ore gave 0.1173 grm. of magnesium pyroarsenate = 49.94 per cent arsenic; (3) 0.2548 grm. of the ore was dissolved in nitric acid, evaporated to dryness, the residue taken up in hydrochloric acid, and the arsenic acid reduced with sulphurous acid. Hydrogen sulphide was then added, the resulting arsenious sulphide filtered off, dissolved in nitric acid, the solution made alkaline with ammonium hydrate, magnesia mixture added, and the arsenic determined as above; 0.2617 grm. of magnesium pyroarsenate was found = 49.72 per cent arsenic.

The insoluble residue remaining after the fusion was dissolved in water was treated with nitric acid and evaporated to dryness. Hydrochloric acid was then added, and hydrogen sulphide passed through the solution for several hours, without the formation of any precipitate of sulphide of arsenic, showing that the mineral must have been completely decomposed.

Nicolite (Ni.As.).—With this mineral the attempt was made to see what effect currents of greater intensity would have on the decomposition. It was hoped that with a current of greater strength the decomposition could be effected in less time, but as will be seen, the results, as far as a diminution of the time limit is concerned, are practically negative.

Two samples of the finely-ground niccolite were subjected to a current which varied from $1\frac{1}{2}$ — $1\frac{3}{4}$ amperes for twenty minutes, and without any reversal of the current, 25–30 grms. of caustic potash being used. In both cases did the residues which remained after disintegrating the fused mass with water show the presence of arsenic, on treating the residues with nitric acid, evaporating to dryness, and the subsequent addition of hydrochloric acid and hydrogen sulphide. The presence of arsenic in the residues is probably due to the fact that the greater strength of current used in the decomposition deposits larger quantities of metallic nickel on the cathode, enclosing at the same time appreciable quantities of undecomposed mineral.

A much weaker current was now tried. Two samples of the mineral were subjected to a current of half an ampere for twenty minutes, 25–30 grms. of caustic potash being used. The result was the same as in the previous case, arsenic being found in both of the residues.

The time limit was now extended with more satisfactory results, the manner of decomposition being as follows:—A current of 1 ampere was allowed to pass through the fused mass for twenty-five minutes, the current passing up through the crucible. At the end of this time the current was reversed for five minutes to remove the metal and any undecomposed mineral that may have attached itself to the platinum wire. The subsequent operations of extracting the alkaline arseniate and weighing it as magnesium pyroarsenate were similar to those already given under gersdorffite, with the exception that instead of filtering the precipitation of magnesium ammonium arseniate through filter-paper, and igniting it in a platinum crucible, the precipitate was filtered directly through a porcelain Gooch crucible, of the pattern recommended by Prof. Caldwell. Owing to the fine, granular condition of the precipitate, this requires some care, particularly if the filter-pump be used. The best results were obtained by first placing a layer of glass wool in the crucible and covering this with a layer of asbestos. After filtering, the crucible with its contents was first dried on a hot plate until all moisture was removed, and then gradually heated over a Bunsen burner

for an hour. In this time all the precipitate will be converted into magnesium pyroarsenate. It is hardly necessary to state that the flame from the burner should not be allowed to enter the crucible below, lest a partial reduction of the precipitate ensue. It was also found advisable to allow the crucibles to stand for twelve hours after ignition, since the constant change in temperature made appreciable differences in the weighings. The results were as follows:—0.1209 grm. of niccolite gave 0.1301 grm. of magnesium pyroarsenate = 52.09 per cent arsenic; 0.1540 grm. of niccolite gave 0.1672 grm. of magnesium pyroarsenate = 52.55 per cent arsenic.

The residues left after disintegrating the fusions gave no reactions for arsenic. They both had a peculiar crystalline appearance resembling minute plates. They dissolved in nitric acid without any evolution of nitrous fumes, and are probably oxide of nickel.

Another sample of the ore was dissolved in nitric acid, the excess of acid evaporated, ammonium hydrate added along with magnesia solution, and the arsenic determined in the usual manner as magnesium pyroarsenate, the weighing being made in a platinum crucible, with the following result:—0.2611 grm. of niccolite gave 0.2833 grm. of magnesium pyroarsenate = 52.52 per cent arsenic.

Arsenopyrite (Fe.As.S).—The conditions under which arsenopyrite is decomposed are very similar to those of niccolite. The quantity of caustic potash used, the time of decomposition, the reversal of the current, &c., are precisely the same, the only difference between them lying in the fact that in the decomposition of arsenopyrite it was found that the current might vary from $1\frac{1}{2}$ amperes without affecting the decomposition. The method of determining the arsenic, as far as the Gooch crucible, &c., is concerned, was the same as under niccolite. Results as follows:—

0.2168 grm. of arsenopyrite gave 0.1729 grm. of magnesium pyroarsenate = 38.6 per cent arsenic.

0.1709 grm. of arsenopyrite gave 0.1356 grm. of magnesium pyroarsenate = 38.41 per cent arsenic.

The residues from the fusions, treated similarly to those under niccolite, showed no traces of arsenic.

0.2306 grm. of the ore were dissolved in concentrated nitric acid, evaporated to dryness, treated with hydrochloric acid and water, and any insoluble matter remaining filtered off. The solution was then reduced with sulphurous acid, the excess removed by boiling, and the arsenic precipitated by hydrogen sulphide. The solution was then allowed to stand until the odour of hydrogen sulphide was barely perceptible, and then filtered on a porcelain Gooch crucible, washed with cold water, carbon disulphide, and alcohol, dried at 100° C. and weighed. The result was 47.73 per cent As. As the high result could be due to but one cause, viz., the presence of sulphur in the precipitate, repeated treatments with carbon disulphide and alcohol were given the latter, but without avail. The precipitate was eventually dissolved in nitric acid, and the arsenic thrown out with magnesia solution. Found: 0.1856 grm. of magnesium pyroarsenate = 38.96 per cent arsenic.

It will be seen from this that the determination of arsenic directly as arsenious sulphide by weighing on a porcelain Gooch crucible is not practicable. The method was tried with various other minerals, and in but one case was the result within limits, due more to accident than to any virtues of the method. The difficulty seems to lie in the fact that the precipitate settles very compactly in the crucible, and prevents the carbon disulphide from obtaining more than a surface contact with it. In some instances the crucible was placed in a beaker, covered with carbon disulphide, and allowed to stand for twenty-four hours without any appreciable difference becoming manifest in the result.

Metallic Arsenic (As).—In the oxidation of the metallic arsenic a difficulty was encountered which the previous minerals had been free from. It was noticed that if the

conditions previously mentioned were followed, viz., that the caustic potash be brought to a state of fusion, and the powdered mineral added, a volatilisation of some of the arsenic invariably occurred. In fact, so rapidly did this take place that barely did the mineral come in contact with the fused potash but what the garlicky odour of arsenic was perceptible. To obviate this loss the following method was found to be the best, and, in fact, the only one that would give accurate results. The caustic potash was introduced into the crucible, carefully heated to drive out all moisture, and eventually brought to complete fusion. The flame was now removed, and the mass allowed to cool until it was almost solid, when the powdered arsenic was carefully spread over the surface of the potash. The platinum wire is now placed in position and the current closed. Should the potash have cooled to such an extent that the current will no longer pass through the mass, or at least only with difficulty, a very small flame carefully played under the crucible will remedy the trouble. The arsenic, if these directions are complied with, becomes gradually oxidised, and no volatilisation is perceptible. After the first ten minutes the crucible may be gently heated until its contents are again in a condition of fusion, and should be kept in such a state until the end of the oxidation. The current used for the operation registered 1 ampère in the Kohlrausch ampèremeter, when the potash was completely fused. At the beginning of the oxidation the resistance offered by the almost solid caustic potash is so great that the current barely registers, but this is exactly the condition that is desirable for thorough results. The current was allowed to run for thirty minutes, being reversed for the last five minutes. The results are as follows:—

0.0974 grm. of arsenic gave 0.1813 grm. of magnesium pyroarsenate = 90.11 per cent arsenic.

0.1052 grm. of arsenic gave 0.1961 grm. of magnesium pyroarsenate = 90.23 per cent arsenic.

The very slight residues which remained after the fusions were treated with water showed no signs of arsenic. The filtrates from the precipitations with magnesia solution were acidulated with hydrochloric acid and hydrogen sulphide added, to see if possibly some of the arsenic might be present as arsenious acid. No trace of the latter, however, was found.

Another sample of the powdered metal was dissolved in nitric acid, and the arsenic determined in the manner already indicated for the previously mentioned minerals, as magnesium pyroarsenate. It yielded 90.14 per cent arsenic.

In the two determinations of arsenic in the metallic arsenic, given above, the magnesium pyroarsenate was weighed on porcelain Gooch crucibles.

Rammelsbergite ($\text{Ni.Co.Fe.})\text{As}_2$.—With this mineral more difficulty was encountered than with any other, and the results that are given below were obtained only after seventeen attempts at decomposition proved unsuccessful. The method used at first was the one which showed itself to be efficient for the decomposition of metallic arsenic, viz., 25–30 grms. of caustic potash and a current of 1 ampère running for thirty minutes, with five minutes reversal at the end of the oxidation. This proved an utter failure, as the residues from the fusion showed in all cases the presence of arsenic, while the results obtained varied from 53–67 per cent of arsenic. A former experience having shown that the non-oxidation might probably be due to the enclosure of particles of mineral on the platinum wire, a more frequent reversal of the current was tried. Using the same amount of caustic potash, and increasing the current strength from 1–1½ ampères, the current was reversed after the first ten minutes, and allowed to run in the opposite direction for three minutes. It was then passed up through the crucible again for five minutes, then again down through the platinum wire for three minutes, the process being continued for thirty minutes. The results were altogether unsatisfactory, large quantities of arsenic being found in the residues.

The amount of caustic potash was now increased from 25–30 grms. to 40 grms., the nickel crucible used being 1½ inches high and 2 inches wide. In six decompositions made under these conditions, the current in the first two had a strength of 1 ampère, in the second two of 1½ ampères, and in the last two it was increased to 1½ ampères, the current being reversed in a manner similar to the one previously tried. The results in all cases were of a negative order, as arsenic was found in all the residues. An increase of the time limit was now tried with satisfactory results. Using 40 grms. of caustic potash the current was allowed to act for forty-five minutes. After various attempts to ascertain the best current strength for the purpose, it was found that a current that registers an ampère was the most satisfactory, and it should not be allowed to rise above this point, otherwise the decompositions are apt to be incomplete. In the oxidations given below, the current was reversed at the end of every ten minutes, for three minutes. Another phase of the operation that seems to be essential is to have the mineral in as fine a condition as possible. Using the conditions just given the residues from the fusions showed no arsenic, though they were most carefully examined by the wet method and also before the blowpipe. The arsenic was precipitated as magnesium ammonium arseniate and weighed as magnesium pyroarsenate in a platinum crucible, the filter being ignited separately after moistening with ammonium nitrate.

The results found were as follows:—0.1829 grm. of rammelsbergite gave 0.2598 grm. of magnesium pyroarsenate = 68.76 per cent arsenic; 0.2168 grm. of rammelsbergite gave 0.3118 grm. of magnesium pyroarsenate = 69.62 per cent arsenic.

Another sample of the mineral dissolved in nitric acid and determined as magnesium pyroarsenate gave 70.34 per cent arsenic.

Chloanthite ($\text{Ni.Co.Fe.})\text{As}_2$.—The mineral used for decomposition was a portion of the sample from Franklin, N.J., which was reported along with other minerals by Dr. Koenig in the *Proceedings of the Academy of Natural Sciences of Philadelphia*, 1889, 184. The decompositions were made contemporaneously with those of rammelsbergite, and for this reason many of the unsuccessful steps which were made with the latter mineral were also made with the chloanthite. The first oxidations were made with a current of one ampère, using 25–30 grms. of caustic potash and allowing the current to run for thirty minutes. As with the rammelsbergite, so here, too, only diverse results were obtained. Reversing the current every five minutes, after the first ten minutes, brought about a similar condition of affairs. The results were from 5 to 6 per cent low. The addition of copper oxide, as recommended by Dr. Smith in the oxidation of pyrites (*Journal of the Franklin Institute*, proceedings of the Chemical Section, vol. ii, p. 62), was now tried. The quantity of caustic potash used being increased at the same time with one sample of the chloanthite, an equal amount of copper oxide was mixed, and with another sample double the quantity of copper oxide. The other conditions were a current of 1½ ampères, a time limit of thirty minutes, with reversals of the current after the first fifteen minutes, and 40 grms. of caustic potash. This combination of conditions gave no better results than the previous one. Satisfactory results were eventually obtained under the following conditions, the copper oxide being dispensed with entirely:—The current was not allowed to register above 1 ampère, and the best results will be obtained if it is kept slightly below this mark. Thirty minutes was found to answer for complete decomposition, but for the sake of certainty it is advisable to allow the current to run for forty-five minutes, reversing it during the last five minutes. The amount of caustic potash used was 40 grms. The results obtained were as follows:—0.2332 grm. of chloanthite was decomposed as above. The fusion was treated with hot water and filtered. The filtrate was acidulated with hydrochloric

acid and warmed to expel the carbon dioxide present. On cooling, the arsenic was reduced with sulphurous acid, and after the expulsion of the excess of sulphurous acid, was precipitated with hydrogen sulphide in the cold. The precipitate of arsenious sulphide was filtered in a Gooch crucible after the solution had stood until it barely had the odour of hydrogen sulphide, and washed with cold water. The crucible and its contents were then placed in a beaker, carbon disulphide added, and allowed to stand twenty-four hours. The crucible was then removed from the beaker, its contents washed with alcohol, then with cold water, and finally dried for six hours at 105°C .; 0.2710 grm. of arsenious sulphide was found = 70.84 per cent arsenic; 0.2899 grm. of chloanthite treated in the same manner as the preceding gave 0.3325 grm. of arsenious sulphide = 69.93 per cent arsenic.

In the sample of the mineral analysed by Dr. Koenig and reported by him he found 70.66 per cent arsenic.

As will be seen from the above, accurate results were obtained by weighing the arsenic as arsenious sulphide. They are, however, but two out of a large number of determinations that were made in porcelain Gooch crucibles, and the only two which gave results sufficiently close to be utilised. The amount of sulphur precipitated with the arsenious sulphide must have been very small, otherwise the results, owing to the inefficacy of the carbon disulphide, would assuredly have been high. For this reason the author cannot recommend the method for general use.

The residues from the fusions were carefully examined for arsenic, but none was found to be present.

Smaltite (Co.Ni.Fe.) As_2 .—From the experience gained with rammelsbergite and chloanthite, it was found very easy to oxidise the smaltite. The mineral used for the purpose was mixed with gangue, and therefore was first broken up, and the smaltite picked out as carefully as possible by hand. The resultant material, as shown by the analyses, still contained impurities. The conditions for oxidation are as follows:—A current of 1 ampère with the restrictions imposed under chloanthite, a time limit of forty-five minutes, and 40 grms. of caustic potash. Using those conditions the oxidation is complete, the residues showing not the least trace of arsenic. The results obtained were as follows:—

0.2233 grm. of smaltite gave 0.2813 grm. of magnesium pyroarsenate = 60.98 per cent arsenic.

0.1790 grm. of smaltite yielded 0.2199 grm. of magnesium pyroarsenate equalling 59.47 per cent arsenic.

The method of procedure resembled one already given. The fusion was acidified with hydrochloric acid, then made alkaline with ammonium hydrate, and the arsenic precipitated with magnesia solution, being finally weighed in a platinum crucible. In the latter of the two determinations, the garlic odour of arsenic was noticeable on igniting the filter paper, although it had previously been thoroughly saturated with a concentrated ammonium nitrate solution. This accounts for the slightly low result obtained, but it was not thought necessary to repeat the operation, since the residue showed that the oxidation was complete.

0.3136 grm. of the ore, dissolved in nitric acid, and the arsenic determined as magnesium pyroarsenate, in a platinum crucible, gave 0.3929 grm. of magnesium pyroarsenate, equals 60.65 per cent arsenic. The difference in percentage from the theoretical amount is due to the impurities in the mineral.

A study of the composition of rammelsbergite, chloanthite, and smaltite will show several points of interest. It will be seen from their formulæ that they each contain two atoms of arsenic to the molecule, while niccolite, cobaltite, arsenopyrite, &c., either have one atom of arsenic to the molecule, or have one atom of arsenic replaced by sulphur. Returning to the study of the conditions necessary for oxidation, it will be remembered that the amounts of caustic potash necessary, and the extents of time, were

larger for the first three minerals than for any of the others, while the oxidations seem to proceed with greater difficulty. A cause for this that might be advanced, is that the oxides of the metals are united with greater tenacity to two arsenic atoms than they are to one, and require a greater expenditure of force for their separation. A somewhat similar occurrence was noticed by Dr. Smith in the oxidation of the metallic sulphides. Pyrrhotite, whose formula is in all probability either $\text{Fe}_{11}\text{S}_{12}$ or FeS , is decomposed with great readiness, while pyrite, which contains two atoms of sulphur to the molecule, succumbed only after repeated and many fruitless trials. What might be considered a curious feature in the oxidation of these arsenides is the fact that those containing two atoms of arsenic to the molecule are decomposed more readily by weak currents than they are by strong ones, while with the arsenides containing but one atom to the molecule, either strong or weak currents are equally efficacious. The only explanation that there is to offer for this seeming anomaly, is the one already given, viz., the enclosure of particles of metal on the platinum wire. In those arsenides containing but one atom of arsenic to the molecule, the decomposition is in all probability so rapid that any enclosure of the mineral on the wire is practically impossible. In minerals like rammelsbergite and chloanthite we may assume that the decomposition proceeds by much slower stages, so that if the current is sufficiently strong to deposit metal on the cathode there is constantly present sufficient undecomposed mineral to be enclosed in the deposited metal.

Cobaltite (Co.Fe.) As_2S .—This mineral was decomposed with great ease,—a result to be expected if we trace the similarity in composition between it and such minerals as gersdorffite, niccolite, &c. The conditions for oxidation are very similar to those of gersdorffite, with the difference that while, in the latter, the current was allowed to run only for twenty minutes, in the decomposition of cobaltite it ran for thirty minutes, with a five minutes reversal at the end. Otherwise the conditions for oxidation and for the subsequent decomposition of the fusion and the estimation of the arsenic, are the same as for gersdorffite. The magnesium pyroarsenate was weighed in platinum Gooch crucibles, the method being very accurate, owing to the fact there is no possibility for any volatilisation of the arsenic, and more rapid than weighing in a porcelain Gooch crucible, since the platinum crucible attains a constant temperature in a very short period of time. The results obtained were as follows:—

0.1032 grm. of cobaltite yielded 0.1006 grm. of magnesium pyroarsenate = 47.2 per cent arsenic.

0.1326 grm. of cobaltite yielded 0.1313 grm. of magnesium pyroarsenate = 47.93 per cent arsenic.

0.2250 grm. of the same ore was dissolved in nitric acid, the acid evaporated, the solution made alkaline with ammonium hydrate, and the arsenic precipitated with magnesia solution. The resultant magnesium ammonium arsenate was ignited in a porcelain Gooch crucible and gave 0.2229 grm. of magnesium pyroarsenate = 47.96 per cent arsenic.

(To be continued.)

Society of Arts.—In consequence of the illness of Prof. W. C. Unwin, F.R.S., the Howard Lectures on "The Development and Transmission of Power from Central Stations," which he was announced to deliver on February 5th and five following Friday evenings, has been postponed.

The Determination of Creatinine in Urine.—J. Moitessier.—Nothing can be effected by methods for determining creatinine founded upon its direct precipitation from urine, in the state of a double zinc-creatinine chloride. Neubauer's method, though tedious and delicate, is exact, and is the only one which can be safely used.—*Bull. Soc. Chim. de Paris.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

December 17th, 1891.

Dr. W. H. PERKIN, F.R.S., in the Chair.

(Concluded from p. 48).

85. "The Sulphochlorides of the Isomeric Dibromonaphthalenes. (I)." By HENRY E. ARMSTRONG and E. C. ROSSITER.

Many statements are on record with reference to the dibromonaphthalenes which are difficult to reconcile; the preparation of characteristic derivatives which could be made use of in distinguishing the various modifications is therefore of importance, and the more they are studied the more is this found to be the case; indeed, more than usual difficulty attends their investigation, as little or no reliance can be placed either on appearance or melting-point, a slight impurity sufficing to produce most misleading changes in these; moreover, the separation of isomerides is made very difficult by their tendency to crystallise together, forming mixtures which simulate pure substances in a most remarkable manner. Unfortunately, also, at the high temperatures requisite to effect the hydrolysis of many of their sulphonic acids, slight decomposition takes place, in consequence of which an impure product is obtained.

Eight of the ten possible dibromonaphthalenes have been prepared, only the 1:1'- $\alpha\alpha$ - and the 2:3- $\beta\beta$ -modifications being unknown. Five of the modifications are referred to in the present notice, viz.:—

1:4-Dibromonaphthalene, prepared by brominating naphthalene.

1:4'-Dibromonaphthalene, prepared from Guareschi's bromonitronaphthalene by reducing, diazotising, &c.

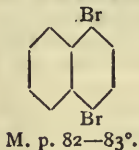
1:3-Dibromonaphthalene, prepared by Meldola's method.

1:2'-Dibromonaphthalene, prepared by brominating β -bromonaphthalene.

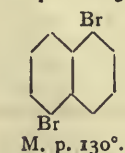
1:3'-Dibromonaphthalene, prepared by the action of PBr_5 on the bromosulpho-acid obtained from the Dahl modification of β -naphthylaminesulphonic acid.

These dibromonaphthalenes are readily sulphonated by heating with twice their weight of H_2SO_4 (so-called 100 per cent acid) on the water-bath until dissolution is complete; on adding potassium carbonate in slight excess to the moderately dilute solution of the sulpho-acid, the potassium sulphonate separates almost entirely from the liquid, and, after re-crystallisation, is converted into sulphochloride.

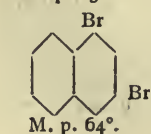
The properties of the sulphochlorides are summarised in the following table:—



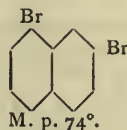
Yields only one sulphonic acid.
 SO_2Cl , prismatic needles; m. p. 120°.



Yields only one sulphonic acid.
 SO_2Cl , prismatic needles; m. p. 175°.

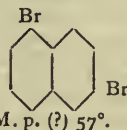


Yields two sulphonic acids.
 α - SO_2Cl , prisms or highly refractive stumpy crystals; m. p. 157°.
 β - SO_2Cl , prismatic needles or long flexible plates; m. p. 128°.



Only one sulphonic acid isolated as yet.

SO_2Cl , prismatic needles which, like the corresponding dichloro-derivative, become opaque on keeping; m. p. 113°.



Only one sulphonic acid isolated as yet.

SO_2Cl , massive prisms; m. p. 145°.

It was stated by Armstrong and Wynne, in 1886 (these *Proceedings*, p. 233), that when 1:3'-naphthalenedisulphonic acid is treated with bromine, it affords a dibromo- β -monosulphonic acid isomeric with that prepared by Jolin from naphthalene- β -sulphonic acid; this conclusion was based on the production from the acid by hydrolysis of a dibromonaphthalene of much lower melting-point than the 1:4-modification, and altogether different from it in appearance: it is now found that the product of hydrolysis in question was impure 1:4-dibromonaphthalene, and it follows, therefore, that the acid from which it was derived is identical with Jolin's.

It is to be noted that whereas the dibromonaphthalenes all have higher melting-points than the corresponding dichloronaphthalenes, no such relation obtains between the sulphochlorides of corresponding dichloro- and dibromonaphthalene.

86. "The Action of Alcohols on Sulphonic Chlorides as a Means of Producing Ethereal Salts of Sulphonic Acids." By HENRY E. ARMSTRONG and E. C. ROSSITER.

It is customary to prepare ethereal salts of sulphonic acids by the interaction of the silver salt and the bromide or iodide of a carbonyl radicle. The authors find that several, but by no means all, of the dibromonaphthalene-sulphochlorides may be converted into the ethereal salt by boiling with ordinary dehydrated alcohol; the 1:4-sulphochloride especially is remarkable for the readiness and completeness with which it undergoes this change, but a small proportion being hydrolysed and converted into sulphonic acid. The 1:4'-sulphochloride under similar conditions is entirely hydrolysed; its behaviour thus affords a striking contrast to that of the 1:4-compound, especially as both are β -sulphonic derivatives. The 1:2'-sulphochloride, which is an α -sulphonic derivative, also yields ethereal salts when boiled with alcohols, although in relatively small amount; this is a further proof that the formation of ethereal salts is not a function of the β -sulphonic radicle.

The peculiar behaviour of the 1:4-sulphochloride is of interest in connection with Heller's observation (these *Proceedings*, 1889, 121) that 1:4-dibromo-, dichloro-, and chlorobromo-naphthalenes behave in a peculiar manner on treatment with SO_3HCl , being converted into sulphones, whereas isomeric compounds yield sulphonic acids as chief product.

It is proposed to study the behaviour of a number of typical sulphochlorides towards alcohols and sodium derivatives of alcohols.

*87. "The Action of Bromine on α - and β -bromonaphthalene." By HENRY E. ARMSTRONG and E. C. ROSSITER.

It is well known that when naphthalene is submitted to the action of two molecular proportions of bromine, a product is obtained from which a considerable amount of 1:4-dibromonaphthalene may be separated without difficulty by crystallising from alcohol, leaving as major product a substance melting at 68—70°; numerous unsuccessful attempts have been made to determine the nature of this product, and although Magatti and also Guareschi have separated a small quantity of 1:4'-dibromonaphthalene from it, down to the present time its constitution has remained a mystery.

As β -dibromonaphthalene is formed in small quantity on brominating naphthalene, the action of bromine on this compound was first studied; it is found to afford 1:2'-dibromonaphthalene almost as sole product.

To determine the nature of the product of low melting-point from naphthalene and two molecular proportions of bromine, it was sulphonated, and attempts were made to effect a separation by re-crystallising the potassium salt of the resulting acid; as these were unsuccessful, sulphochloride was prepared: by crystallising this from benzene and from acetic acid, a considerable fraction of the product was ultimately recognised as the sulphochloride of 1:4-dibromonaphthalene. The residual sulphochloride melted at 107–110°; numerous attempts were made to purify this by crystallisation without success; it was hydrolysed at 260–270°, but the product had a low melting-point and could not be identified; but on boiling it with alcohol a considerable amount of the ethylic salt of 1:4-dibromonaphthalenesulphonic acid was obtained. It was, therefore, evident that on brominating naphthalene much more 1:4-dibromonaphthalene is formed than is commonly supposed. Fresh attempts were then made to resolve the crude product melting at about 70° into its constituents by means of solvents. Eventually, on fractionally extracting it with light petroleum, it was found that the first separations from the last extracts melted at 115–125°, and on crystallising this product from alcohol, it melted at 129–130°, and was identified as 1:4'-dibromonaphthalene.

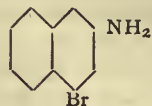
A small quantity of 1:4-dibromonaphthalene was obtained from the first extractions by petroleum; the rest of the product melted at 68–70°. On crystallising this latter from alcohol a further separation of 1:4-dibromonaphthalene was obtained, but the residue still melted at 68–70°. However, by alternately crystallising this last product from petroleum and alcohol, it was gradually split up into 1:4- and 1:4'-dibromonaphthalenes, the melting-point of the residue always remaining constant at 68–70°.

From these results it is concluded that the substance melting at 68–70° is a mixture of 1:4- and 1:4'-naphthalene, and from the weights obtained of these it is concluded that the 1:4-dibromonaphthalene constitutes about four-fifths and the 1:4'-one-fifth of the mixture.

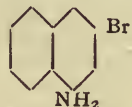
No 1:3-dibromonaphthalene was obtained. As a mixture of 1:4- and 1:3-dichloronaphthalenes is obtained by the action of chlorine on naphthalene, the production of the 1:4- and 1:4'-compounds by the action of bromine would seem to be an indication of a great difference between the action of chlorine and bromine on naphthalene; but such is not the case. The formation of the dichloronaphthalenes is preceded by that of a comparatively stable tetrachloride, but no such compound is produced by the action of bromine; probably a highly unstable dibromide is first formed, which is at once resolved into hydrogen bromide and bromonaphthalene, and the latter is then further acted on. Experiments, of which an account will be given later on, show that when chloronaphthalene is chlorinated results are obtained very similar to those obtained on brominating bromonaphthalene.

*88. "The Action of Bromine on a Mixture of Ortho- and Paranitro- α -acenaphthalide." By HENRY E. ARMSTRONG and E. C. ROSSITER.

Meldola, in 1885 (*Trans.*, pp. 497–518), described two series of compounds derived, one from brominated α -acenaphthalide, the other from nitrated acenaphthalide; the former was converted by nitration into nitrobromacenaphthalide, from which the amido-group was eliminated, and the resulting nitrobromonaphthalene was reduced, a bromonaphthylamine being thus obtained, which, judging from previous observations, must necessarily be the compound of the formula—



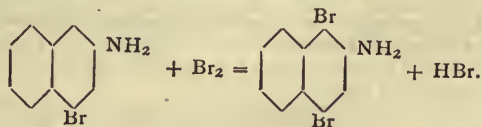
Nitrated acenaphthalide was known to be a mixture of the ortho- and para-derivatives; by brominating the mixture Meldola obtained a single product which he supposed to be derived from the *para*-constituent, and therefore he regarded the bromonaphthylamine obtained by eliminating the amido-group and then reducing as the isomeride of that prepared from bromacenaphthalide, viz., as—



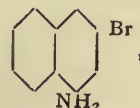
From the bromonaphthylamines from the two sources, Meldola prepared dibromonaphthylamines, from which he then prepared dibromonaphthalenes, obtaining in this way a modification melting at 74° from each source. Some time after the appearance of his paper (*cf.* these *Proceedings*, 1886, 172), he was led to modify his views of the constitution of the compounds he had obtained in consequence of the discovery by Stallard that the bromophthalic acid which Meldola prepared by oxidising one of his dibromonaphthylamines was derived from an α - and not from a β -bromonaphthalene; Meldola therefore suggested that the one amine was the compound $\text{NH}_2:\text{Br}:\text{Me}=2:4:1'$, and the other the compound $\text{NH}_2:\text{Br}:\text{Me}=1:3:3'$ or $1:3:2'$.

Wishing to prepare the 1:1'-dibromonaphthalene, the authors proceeded to repeat Meldola's work, as the argument which he made use of appeared to be a sound one, and there was, therefore, reason to think that the dibromonaphthalene which he had obtained starting from brominated acenaphthalide was the 1:1' modification; that obtained from the other source the authors were inclined to expect would prove to be the 1:2'-modification, which is known to melt at 74°.

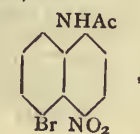
On preparing the two bromonaphthalenes in accordance with Meldola's directions, products were obtained, however, which both melted at 82–83°, the identity of which with 1:4-dibromonaphthalene was placed beyond doubt by conversion into the sulphochloride melting at 118° to 120° and the ethylic sulphonate melting at 156–157°. The production of 1:4-dibromonaphthalene from the bromonaphthylamine prepared from nitrated parabromacenaphthalide is easily understood, thus—



Its production from a bromonaphthylamine of the formula—



however, is clearly impossible; but it was conceivable that a heteronuclear derivative is formed on brominating paranitracenaphthalide, viz.:—



In this case the bromonaphthylamine obtained on eliminating the NHAc group and reducing should be convertible into 1:1'-dibromonaphthalene; according to Meldola it yields 1:3-dibromonaphthalene, but he was led to form this conclusion only by the appearance and melting-point of the product. The authors have prepared the dibromonaphthalene in question, and have proved it to be the 1:3-compound, as stated by Meldola, by converting it into the two sulphochlorides melting at 127° and 157° characteristic of this modification; and by completely reducing the bromonaphthylamine in question they have obtained β -naphthylamine.

There appears to be but one explanation possible of these results, viz., that when a mixture of ortho- and paratracenaphthalides is brominated, the ortho-compound—not the para-, as Meldola supposed—is alone attacked, and that consequently the same nitrobromonaphthalene is obtained on displacing the acetamido-group in nitrated parabromo- α -acenaphthalide, and in the product of the action of bromine on a mixture of the ortho- and paratracenaphthalides.

Meldola, although struck with the remarkable similarity of the two series of compounds which he prepared, was led to notice certain differences: thus he obtained bromonaphthylamines melting, the one at 71.5°, the other at 62°; but the authors find that both products melt at 72°, and that the dibromonaphthylamines prepared from them melt at the same temperature, viz., 106°. Messrs. Miers and Pope have examined a number of the pairs of products, and report that corresponding compounds are not only identical in form, but also in optical properties, and as no case is on record of different substances being alike both morphologically and optically, there can be no doubt of the correctness of the explanation now advanced.

*89. "*Camphrone, a Product of the Action of Dehydrating Agents on Camphor.*" By HENRY E. ARMSTRONG and F. S. KIPPING.

The action of concentrated sulphuric acid on camphor appears to have been first examined by Chautard; it was subsequently studied by Fittig, Schwanert, and Kachler, all of whom agree in stating that under suitable conditions an oily product, having a strong peppermint odour, is formed, isomeric with acetophorone, $C_{15}H_{14}O$, which consequently has figured in chemical literature under the name *camphorone*. The various statements regarding the properties of this substance, however, are by no means confirmatory, Fittig stating that it boils at 204–205°, and that it has a relative density of 0.939 at 12°, whereas Schwanert gives 230–235° as its boiling-point and 0.9614 at 20° as the relative density.

Armstrong and Miller noticed the presence of a substance having properties similar to those of the product obtained by means of sulphuric acid among the products of the action of zinc chloride on camphor; but attempts which they made to isolate a definite substance from their crude product were unsuccessful.

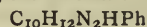
It appeared probable that, with the aid of the improved methods of treating ketonic compounds now known, it would be possible to separate the characteristic constituent from the crude oil, and this has proved to be the case.

On treating the fraction boiling at 238–242° of the oil prepared by means either of sulphuric acid or of zinc chloride with phenylhydrazine, a mixture of a crystalline hydrazone with dark coloured oily products is obtained; the purified hydrazone crystallises in yellowish plates and melts at about 108°. By boiling it in alcoholic solution with ferric chloride and muriatic acid, an oil is obtained which yields a hydrazone identical with that from which it was prepared; on distilling this oil the thermometer rapidly rises to 245°, the greater part of the liquid passing over at 245–247°. On treatment with hydroxylamine the oil is converted into a hydroxime which crystallises in long prisms melting at 85–86°, of which the acetyl derivative melts at 69–70°.

The determination of the composition of these compounds presents considerable difficulty; analyses of the oil gave the following results:—

Carbon, per cent.	80.84	80.88
Hydrogen, „	8.13	8.14

—numbers which agree satisfactorily with the formula $C_{10}H_{12}O$. But in numerous analyses of the hydroxime, the carbon was found to vary from 72.4–72.8 per cent; hydrogen from 7.8–8.0 per cent; and nitrogen from 8.6–8.9 per cent: these values do not agree with those required by a compound of the formula $C_{10}H_{12}N(OH)$, except the nitrogen values ($C=73.6$, $H=7.27$, $N=8.6$). The acetyl derivative of the hydroxime gave similar results. The hydrazone was found to contain 12–12.2 per cent of nitrogen, the calculated value for—



being 11.8. Evidently it is necessary to make a more complete study of the compound to place its composition beyond doubt, especially as the formula $C_{10}H_{12}O$ is a very remarkable one.

On oxidising the oil with nitric acid it yields an acid which crystallises well.

Obviously the substance is one of considerable interest, and its further investigation is likely to throw light on the still open question as to the structure of camphor. As the yield, even of the crude product, is small, and the preparation of the pure substance is a matter of considerable difficulty, it appears desirable to make this preliminary announcement, now that workers are becoming so numerous in this field.

*90. "*Metaxylenesulphonic Acids (II.).*" By G. T. MOODY, D.Sc.

In a previous communication (*Proceedings*, 1888, p. 77), the author has described the preparation of 1:2:3-metaxylenesulphonic acid, and has called attention to the fact that only the 1:3:4-acid is formed on direct sulphonation of the pure hydrocarbon. Attempts to prepare the symmetrical 1:3:5-sulphonic acid have not yet met with success, the sulphonation of 1:3:4-acetmetaxylyl failing to give the required substitution.

Acetmetaxylyl (1:3:4) is readily sulphonated when heated for some time at 140° with 1½ times its weight of 20 per cent anhydrous sulphuric acid, and on boiling the solution after the addition of water, metaxylylidesulphonic acid ($Me_2:NH_2:SO_3H=1:3:4:6$) is obtained. It crystallises from water, in which it is only very sparingly soluble, in well-formed, slender needles, insoluble in alcohol and other common solvents; it does not change at 290°, and when heated to a higher temperature, decomposes without having previously melted. The sodium salt, $C_6H_3Me_2NH_2SO_3Na \cdot H_2O$, is exceedingly soluble in water and crystallises in flat plates.

On diazotising the acid and subsequently boiling the solid product with dehydrated methylated spirit, ethoxy-metaxylenesulphonic acid ($Me_2:OEt:SO_3H=1:3:4:6$) was obtained. The sodium salt of the acid crystallises in long, slender needles, which effloresce when exposed to the air; the sulphochloride crystallises from light petroleum in beautiful orthorhombic plates, melting at 56°; the sulphonamide separates from dilute alcohol in small white scales, or flat needles which melt at 169–170°.

When the diazo-product is boiled with bromhydric acid, the corresponding bromoxylenesulphonic acid ($Me_2:Br:SO_3H=1:3:4:6$) is formed. It crystallises in long slender needles, and does not melt at 270°, but at a considerably higher temperature melts with decomposition. The sodium salt agrees with the description given by Weinberg (*Ber.*, xi., 1062), who obtained it on bromination of a dilute aqueous solution of barium 1:3:4-metaxylenesulphonate; but the sulphochloride obtained by the author, which crystallises in splendid oblique prisms, melts at 2° higher (62–63°), whilst the sulphonamide melts at 5° lower (189°) than found by

Weinberg. The melting-point of the sulphonamide agrees with that given by Sartig (*Annalen*, cccxxx., 335), who prepared it by sulphonating metaxylidine, and subsequently replacing amidogen by bromine. It thus appears that both xylidine and acetylidy give the same acid on sulphonation, and that the displacement of hydrogen in the amido-group by acetyl does not lead to any change in the position taken up by the sulphonic group.

*91. "*The Action of Propylene Bromide on the Sodium Derivatives of Ethylic Acetoacetate and Ethylic Benzoyl-acetate.*" By W. H. PERKIN, Jun., Ph.D., F.R.S., and JAMES STENHOUSE.

The product from ethylic acetate is a mixture of ethylic acetylmethyltrimethylenecarboxylate and ethylic methyl-diacetyladipate. The former is found to yield a well-crystallised hydroxime (m.p. 153–155°); when boiled with water, it is gradually converted into acetoisobutyl alcohol. Ethylic methyl-diacetyladipate is decomposed on distillation into an oil which is a mixture of at least two compounds, as, when hydrolysed, it yields dimethyl-dihydropentenedicarboxylic acid, together with dimethyl-dihydropentene methyl ketone.

Ethylic benzoylmethyltrimethylenecarboxylate and several of its derivatives are also described in the paper.

92. "*Derivatives of Tetramethylene.*" By W. H. PERKIN, Jun., Ph.D., F.R.S., and W. SINCLAIR, B.Sc.

By the action of bromine in presence of phosphorous on tetramethylenecarboxylic acid, the authors have obtained an almost quantitative yield of the monobromo-derivative. They describe its methylic salt, and the corresponding hydroxy-, acetoxy- and ethoxy-acids. By acting on the chloride of the acid with zinc methyl and ethyl, they have prepared tetramethylene methyl and ethyl ketones, of which they also describe the reduction products.

CORRESPONDENCE.

EXPLOSION OF A SODIUM BOTTLE.

To the Editor of the Chemical News.

SIR,—A short time since we had a violent explosion in our laboratory. On investigation it proved to arise from the explosion of a bottle containing about 2 lbs. sodium, which had been as usual preserved in naphtha; it had not been touched for about two years, and possibly the naphtha had evaporated. Can any of your correspondents state the cause of the violent explosion which occurred, scattering the bottle and its contents all over the room? If it had occurred at night it would have been very dangerous; as it was it occurred in the day at a time when no one was present, much of the sodium had ignited. Is there this danger in storing sodium?—I am, &c.,

A. MERRY.

Hafod Isha Works, Swansea.
Jan. 23, 1892.

MELTING SNOW IN THE STREETS.

To the Editor of the Chemical News.

SIR,—There has been this winter the usual crop of inventors who, without the slightest knowledge of the subject they advocate, endeavour to enlist the time and money of others as ignorant as themselves in a very foolish scheme, *i.e.*, to use ordinary gas to melt the snow which obstructs the streets, some of the sanguine having gone to some expense in demonstrating what was already known, *i.e.*, the possibility of it irrespective of cost.

How absurd such a project is can be easily seen by comparing the known heating value of coal-gas with the work to be done.

Six inches deep of average snow, when melted, becomes half an inch depth of water, 24 square feet of which will weigh 62½ lbs., or 23¼ lbs. per square yard. At this rate the snow on one mile (or 1760 yards) of a street 20 yards wide would, if 6 inches deep, weigh 823,680 lbs., or 363½ tons.

The heating power of London gas is 660 units per cubic foot, *i.e.*, one cubic foot of coal-gas will heat 660 lbs. of water 1° F., and of this we may take it as a maximum that 500 units could be utilised.

It has been proved repeatedly and beyond question that 1 lb. of snow at freezing-point requires 150 units of heat to melt it and raise the temperature of the water obtained to 40° F., and this effect would be produced on 3½ lbs. of snow by the consumption of one cubic foot of coal-gas. From the above data it will be found that to melt the snow in the assumed mile of street would require the consumption of 247,000 cubic feet of gas, costing, at 3s. per 1000 cubic feet, a little over £37, or at the rate of £3256 per square mile.

As there are a great many square miles of streets in many towns, and as the snowfall has already been nearly double that assumed, it will be seen that the problem is most certainly not one to be solved by this method. Even if we were to assume that the cost of gas and labour was not prohibitive, the fact that the ground itself is usually colder than 32° must be considered, and the ground would also have to be warmed, or a thin surface of glassy ice, of the most slippery and dangerous kind, would remain after the snow was removed; this alone would condemn the project as being unworthy of consideration.—I am, &c.,

THOMAS FLETCHER, F.C.S.

Warrington.

DISCUSSION AT THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—At the meetings of the London Section of the Society of Chemical Industry, and also, I believe, at those of the Society of Public Analysts, a shorthand writer is employed to report the discussions which take place after the reading of papers. I venture to suggest that the same course be adopted at the meetings of the Chemical Society.

Under the present arrangements, whatever they may be, the reporting can only be described as sketchy. If a discussion is to be printed at all it should surely be printed as it takes place, with the exception of such *lapsus linguæ* as will occur at the Chemical Society and, I suppose, elsewhere.

Moreover, is not a shorthand reporter almost as good a deterrent as it is possible for a president to be?

These remarks are called forth by a perusal of the report of the meeting of December 17th, as printed in your issue of January 22nd.—I am, &c.,

ONE WHO LISTENED.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 2, January 11, 1892.

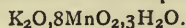
The Spontaneous Oxidation of Humic Acid and of Vegetable Mould.—MM. Berthelot and G. André.—Humic acid, on exposure to light, turns yellow and evolves carbonic acid. No trace of nitric acid has been detected. The same reaction was observed on treating vegetable mould with a cold dilute solution of potassa.

These reactions are purely chemical, not depending on the presence of microbia.

New Observations on the Determination of Sulphur in Vegetable Soil, and on the Nature of the Compounds which it Forms.—MM. Berthelot and André.—Sulphur exists in a constant manner in the composition of vegetable soil, as well as in plants, that is in the state of special organic principles. One kilo. of a certain soil was found to contain:—total sulphur 1.41, sulphur in sulphates 0.18. This organic sulphur can be extracted by means of gaseous chlorine, acting upon the soil in presence of dilute boiling potassa.

The Metallic Borates.—A. Ditte.—Comments on a paper by M. Le Chatelier, relating to the author's researches on the subject.

Hydrated Potassium Manganites.—G. Rousseau.—The author has obtained three definite compounds, well crystallised, on operating at different temperatures. About 600° he obtains $K_2O, 16MnO_2, 6H_2O$; between 700° and 800° there is produced the compound—



Between 800° and 1000° the hydrate, $K_2O, 16MnO_2, 6H_2O$, reappears, and at orange redness there is formed the more condensed hydrate $K_2O, 32MnO_2, 10H_2O$.

Reduction of Benzene Hexachloride with Regeneration of Benzene.—J. Meunier.—The author succeeds in the complete reduction of α -hexachloride. The regeneration of benzene is so easy that it may serve for obtaining this body in state of purity. The reduction is effected by means of zinc and acetic acid.

The Formation of the Dextrines.—P. Petit.—In the dextrines prepared by the Payen process there is formed a matter not fermentible, but reducing Fehling's liquor.

A New Unsaturated Fatty Acid of the Series $C_nH_{2n-4}O_2$.—A. Arnaud.—This fatty acid is found in the seeds of a shrub belonging to the genus *Picramnia*, very common in Guatemala. Its composition is represented by the formula $C_{18}H_{32}O_2$. The author proposes to name it Tariric acid, from a local name of the shrub.

Influence of the Proportions of Clay and Organic Nitrogen on the Fixation of Atmospheric Nitrogen, on the Conservation of Nitrogen, and on Nitrification.—P. Pichard.—This paper will be inserted at some length.

MISCELLANEOUS.

The Weighting of Leather.—W. Eitner (*Der Gerber*).—Leather which has been weighted with glucose and only air-dried is soft on account of the hygroscopic character of the glucose, becomes readily mouldy, and enters into fermentation. This evil is avoided by heating the weighted air-dried leather from 50 to 60° for 6 to 10 hours. The glucose is thus converted into the non-hygroscopic anhydride; at least, the leather thus treated becomes very firm and remains firm on keeping. The glucose may be qualitatively detected, according to Eitner and Meerkatz, by extracting 1 grm. of the finely minced leather for five minutes in 10 c.c. of cold water. The extract is poured off, mixed with recently ignited magnesium oxide, and shaken until the liquid appears decolourised. In this manner tannin and colouring matters which form sugar on subsequent treatment with sulphuric acid and might mask the reactions by turning brown are eliminated. 2 c.c. of the filtrate are mixed with 3 drops of a 15–20 per cent alcoholic solution of α -naphthol and an equal or double volume of concentrated sulphuric acid is then added to the mixture. If glucose is present there appears at once a deep violet-blue colour, and on adding water a blue precipitate is separated (Molisch's reaction). If no glucose is present the liquid, according to the ware

with which the leather was tanned, takes a yellow, orange, or reddish-brown colour. The glucose may be determined quantitatively by Kohnstein's method. Other fraudulent additions to leather are magnesium sulphate, barium chloride, and especially a mixture of magnesium sulphate and glucose. These weighting mixtures are soluble in water and can be readily detected by means of known reactions. But the leathers after being strongly shrivelled are treated for 2 to 3 hours with a concentrated solution of barium chloride, let drain, shrivelled again, placed for some hours in a solution of sodium sulphate, repeating the entire operation several times. In this manner the leather can be weighted with considerable quantities of barium sulphate whilst the sodium chloride formed is extracted. Such leather may be detected by a determination of the ash; the ash of leather is at the utmost 3 per cent, generally only 1. Properties of ash exceeding 3 per cent give proofs of fraud.—*Zeit. Anal. Chemie.*

MEETINGS FOR THE WEEK.

MONDAY, Feb. 1st.—Medical, 8.30.

Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Oxidation of the Acids of the Fatty Series," by Messrs. Wanklyn and Johnstone. "The Stability of Certain Organic Nitrogen Compounds Occurring in Coal-tar Pitch," by Mr. Watson Smith.

TUESDAY, 2nd.—Royal Institution, 3. "The Brain," by Prof.

Victor Horsley, F.R.S.
Institute of Civil Engineers, 8.
Pathological, 8.30.

WEDNESDAY, 3rd.—Society of Arts, 8.

THURSDAY, 4th.—Royal, 4.30.

Royal Society Club, 6.30.
Royal Institution, 3. "Some Aspects of Greek Sculpture in Relief," by A. S. Murray.
Chemical, 8.

FRIDAY, 5th.—Royal Institution, 9. "On Metals at High Temperatures," by Prof. Roberts-Austen, C.B., F.R.S.

Geologists' Association, 7.30. (Anniversary).
Quekett Club, 8.

SATURDAY, 6th.—Royal Institution, 3. "The Induction Coil and Alternate Current Transformer," by Professor J. A. Fleming, M.A., D.Sc.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1680.

AGRICULTURAL CHEMISTRY.

THE ACTION OF ELECTRIC CURRENTS UPON THE GROWTH OF SEEDS AND PLANTS.

By Dr. JAMES LEICESTER,

Lecturer on Chemistry at the Merchant Venturers' Technical School, Bristol.

A.—Zinc plate buried in the soil and about 1 square foot in size.

B.—Plate of copper having the same dimensions as the zinc plate, and connected at the top by a copper wire above the surface (c) with the copper plate (B).

D.—A box about 3 feet long and about 2½ feet wide filled with soil.

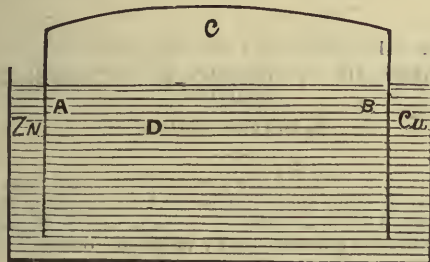


FIG I

By means of the apparatus shown in Fig. I. a weak current can be passed through the soil. The strength of the current will vary with the amount of organic acids in the soil. A series of experiments were conducted with the object of finding out whether these weak currents would in any way affect the growth of seeds and plants. In order that there could be good comparative tests, a number of glass vessels were obtained all of the same size, filled with similar soil, and exposed to the same conditions, such as temperatures and sunlight. In some of these were placed earth plates, as shown in A (Fig. II.), whereas the others only contained the soil. They



FIG II

were watered each day at the same time and with equal quantities of water. Various seeds were obtained, and the same number of seeds sown in both vessels at the same time and under the same conditions. In all cases the seeds grew very much quicker in the vessels containing the earth plates. In the case of hemp seed it was fully an inch above the surface before there was any sign of it in the ordinary vessels.

Larger plates have been made connected as before and buried in the ground a few feet apart. In these larger experiments the same results were obtained. Seeds were sown in drills as shown in Fig. III. Those in the zones, a, b, b', were the first to appear. Next came those in the zones c and c'. Those sown at d and d' came up nearly a week later than the others.

In order to vary this experiment the earth plates were

next buried where d was, and fresh seeds sown. The greatest fertility was then noticed to be in the neighbourhood of d, that is to say, between the two plates.

With regard to plant life experiments are now being conducted, but so far no distinct difference has been noticed in the case of those under ordinary conditions and those with the earth plates. If the soil is watered with a little very dilute acetic acid the growth of the seeds is much quicker in the case of the earth plates, but no difference is noticed in the ordinary vessels. The latter

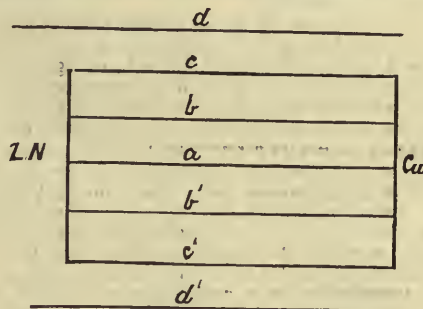


FIG. III

result is probably due to the slight increase in the strength of the current due to the action of the acetic acid.

These earth plates are hardly practicable on a large scale, but might be used in frames or for forcing under glass.

3, Queen's Parade, Brandon Hill, Bristol,
January 16, 1892.

EXAMINATION OF INKS.*

By OSW. SCHLUTTIG and G. S. NEUMANN.

A. Inks of Class I. Prepared with Iron and Galls.

Preliminary Test.—The bottle is opened carefully without shaking, 15 to 20 c.c. of ink are drawn out with a pipette, the bottle being immediately closed again with a cork, air-tight, but so that it can be afterwards uncorked again without shaking. The bottle is then left standing quietly for three days at a temperature of 15°.

Meantime a *type* is prepared of the same colour as the ink under examination. A normal ink is first obtained as follows:—23.4 grms. tannin and 7.7 grms. crystalline gallic acid are dissolved in hot water at 50°, and to this solution, diluted as far as convenient, there is added a solution of 10 grms. gum arabic, and further 10 grms. of "official" hydrochloric acid (containing 2.5 grms. HCl), a solution of 30 grms. ferrous sulphate, and 1 grm. carbolic acid. The whole is well mixed and diluted to 1 litre; it is then allowed to stand for at least four days at 10–15°, when the clear solution is drawn off from the slight deposit formed. Filtration through paper is to be avoided as much as possible in the examination of inks. If it is unavoidable a fine filter-paper must be used which will absorb merely a trace of tannin. This normal ink is then brought to the exact tone of the ink in question by the addition of suitable colouring matters, using as a standard the 15 c.c. first taken out of the bottle.

The colours used by the authors were:—

Blue—Bayrisch blue D.S.F. of the Berlin Company for Aniline Colours.

Red—Nacarat S from the same works.

Green—Acid green V.B.S.Po. of K. Oehler, of Offenbach.

Brown—Chestnut brown from the same works.

* Treatise by Zahn and Jaensch, *Zeit. für Analyt. Chem*

For instance, we may obtain a type of medium intensity with—

Blue.	Green.	Red.	Black.	
2.2 grm.	1.0	—	2.5	} Blue. Green. Red. Brown, per litre.
—	2.5	—	0.5	
—	—	2.5	—	
—	—	—	3.5	

By increasing or diminishing the additions of colouring matters and by combining these various types, all required shades may be obtained.

After three days the bottle is carefully uncorked, and without shaking fully 50 c.c. are taken out of the middle of the liquid with a pipette and filtered through a small folded filter of the finest white filter-paper, taking care that the filtrate does not come in contact with the oxygen of the air more than necessary. Of the filtrate we take exactly 25 c.c. to test its *permanence in glass*. 25 c.c. are let flow into a clean and dry bottle holding 500 c.c. It should be of a cylindrical form, 185 m.m. high and 72 m.m. in diameter, with a flat bottom. The bottle is loosely covered with a cap of filter-paper to exclude dust. The bottle, in which the liquid stands at the depth of about 12 m.m., is allowed to stand for several days at the ordinary temperature of a dwelling-room, is free from ammonia and acid and in diffused light, and is observed. If the bottle is raised up in the hand, shaking must be avoided, as it might cause any film or scum formed on the surface of the liquid to sink to the bottom and be mistaken for a sediment. If at the end of fourteen days any separation takes place, whether on the surface, on the sides of the bottle, or at the bottom, the ink is to be pronounced unsatisfactory from want of permanence.

The type prepared from pure materials remained when submitted to this test three weeks entirely unaltered; there then was formed on the surface of the liquid a film which, even after the lapse of six weeks, was but insignificant. At the beginning of the fourth week a few small points like spots were to be seen at the bottom.

Test for Darkening on Paper.

For this purpose there are used the 15—20 c.c. of unfiltered ink first taken out of the bottle. The test is executed with stripes of ink produced as follows:—A piece of the best white writing paper is stretched tightly and smoothly in a frame placed at an angle of 45°; 0.6 grm. of the ink in question is taken up in a pipette 250 m.m. in inner width and 250 m.m. in length; the mark is at 62 m.m. from the lower end. The pipette is held perpendicularly to the paper, and the ink is allowed to flow out without air-bubbles. There is thus formed a stripe of ink about 6 m.m. wide, and in length, in the author's apparatus, 270 m.m. Such stripes are made side by side with the ink in question and with the type both in their original state, and after each has been diluted with an equal volume of water, in each case three or four times alternately. The frame with the paper is left in its position until the ink has become completely dry upon the paper. The paper is then taken off and left at the common temperature for eight days in air free from dust and acidity and in diffused light. This time is necessary for completing the process of oxidation of the ink. The stripes of undiluted ink are then especially used for judging of the fluidity, the penetration, and the glutinousness, whilst those with the dilute ink serve merely to show the subsequent darkening. If it appears that the dilute ink has not darkened in eight days as much as the dilute type, the ink is pronounced unsatisfactory and no further trial is needed. If the stripes of ink have taken as dark a colour as those of the type, the paper is cut into slips across the direction of the stripes so as to form bands of 3 c.m. in width. One of them is steeped in distilled water, a second in alcohol at 85 per cent, and a third in alcohol at 50 per cent, and allowed to lie for two days. They are then taken out, dried at the

common temperature, and the intensities of the residual stripes of the ink in question and of the type are compared. If the ink is satisfactory the stripes on all the three bands must be as dark as the corresponding stripes of the type.

Examination of Fluidity, Penetration, and Adhesiveness.

The fluidity of an ink is best judged by writing with it. It must also be considered that the point of commencement of the stripes obtained as above described has an oval expansion, and the stripe is then nearly equally broad. In inks which flow from the pen too readily the beginning point is very broad and the stripe then narrows downwards.

Whether an ink strikes through the paper is seen by trial-writing.

For testing an ink for its adhesiveness it is necessary to write upon normal paper with the ink in question as well as with the type. The adhesiveness after drying is compared by the application of the hand or of a piece of paper.

(These tests are, of course, not applicable to inks such as vanadium ink, chrome ink, &c.).

I. THE IODATION OF *p*-BROMOBENZOIC ACID. II. SALTS OF *p*-BROMO-*m*-NITROBENZOIC ACID.*

By OLIVER HOUGH.

It is stated by Weselsky (*Annalen*, clxiv., 99) that the method of iodation recommended by him is not applicable in the case of bromobenzene or benzoic acid. Believing that possibly a different result might be obtained with bromobenzoic acid, in which two hydrogen atoms are replaced by different substituents, the following experiments were made:—

1. Ten grms. of *p*-bromobenzoic acid, dissolved in alcohol, were heated with the calculated amounts of iodine and mercuric oxide. The product was heated with an aqueous solution of sodium carbonate, and filtered while hot. Hydrochloric acid was added to the cold solution, and the liberated organic acid converted into its barium salt. Analysis showed it to be the barium salt of *p*-bromobenzoic acid. The iodation had not been effected.

2. It was suggested that possibly the iodation had really occurred, but that the sodium carbonate had again removed the iodine. To ascertain whether such was really the case, the acid, after treatment, was digested immediately with barium carbonate. The resulting salt proved to be *p*-bromobenzoate of barium.

3. A third experiment was equally fruitless. Finally, the *p*-bromo-acid, in alcoholic solution, was heated together with iodine and mercuric oxide, in a sealed tube. The temperature of the oven was 150° C. Iodine was not introduced into the acid even in this way.

I. SALTS OF *p*-BROMO-*m*-NITROBENZOIC ACID (M.P. 199° C.)

The known salts of this acid are those of barium, magnesium, and silver. The following are new:—

The *potassium salt* forms yellow coloured prismatic needles, varying in length from one-half to one inch. One hundred parts of water at 26° C. dissolve 33.44 parts of the salt. The salt is anhydrous.

The *sodium salt* crystallises in needles. It contains one molecule of water of crystallisation; 100 parts of water at 26° C. dissolve 16.01 parts of the salt.

The *ammonium salt* separates from aqueous solutions in anhydrous needles; 100 parts of water at 26° dissolve 12.22 parts of the salt.

The *strontium salt* consists of minute white needles. It

* Read at the Chemical Section of the Franklin Institute, October 20, 1891.

contains $3\frac{1}{2}$ molecules of water of crystallisation. Found 14.88 per cent Sr instead of 15.10 per cent; 100 parts of water at 26° dissolve 0.88 part of the salt.

The calcium salt consists of white needles. The air-dried salt lost, when carefully heated in an air-bath at 160°, 30.25 per cent of water, corresponding to thirteen molecules. Found 7.45 per cent Ca instead of 7.54 per cent; 100 parts of water at 26° dissolve 1.09 parts of the salt.

The zinc salt crystallises in white needles; 100 parts of water at 24° C. dissolve 0.70 part of the salt. The addition of zinc chloride to a solution of potassium nitro-bromobenzoate, produced a white precipitate which crystallised from hot water in round yellow coloured masses. Under the microscope these appeared to consist of bundles of little plates. An analysis of the salt showed it to be the basic zinc salt. It contains three molecules of water. Found zinc = 20.24 per cent instead of 19.87 per cent.

The mercury salt is anhydrous and white in colour; 100 parts of water at 26° dissolve 0.96 part of the salt. Found Hg = 44.04 per cent instead of 44.90 per cent.

The nickel salt crystallises in light green coloured crusts; 100 parts of water at 26° dissolve 1.47 parts of the salt. It contains $2\frac{1}{2}$ molecules of water.

The cobalt salt consists of pink needles. It contains three molecules of water; 100 parts of water at 26° C. dissolve 1.05 parts of the salt. Found 11.53 per cent Co instead of 10.74 required.

I carried out the above work in the laboratory of Dr. Edgar F. Smith, University of Pennsylvania.

DISTRIBUTION OF TITANIC OXIDE UPON THE SURFACE OF THE EARTH.*

By F. P. DUNNINGTON,
University of Virginia, Charlottesville, Va.

At the Ann Arbor meeting of the Association for the Advancement of Science in 1885, I read a short paper (*Proceedings A. A. S.*, xxxiv., 132), which considered the occurrence of titanic oxide in considerable amount in certain soil of Albemarle Co., Va.; and in an article published (*Amer. Chem. Journ.*, x., 36) in 1888, by Mr. J. F. McCaleb and myself, we presented estimations of this substance in sixteen specimens of soil from scattered points of the United States.

In view of the unfrequent mention of this element as a constituent of rocks and the very rare mention of its occurrence in soils, I have endeavoured to secure samples of soil and some rocks from points scattered over the earth's surface; and, including the before mentioned sixteen, I herewith present the results of examining eighty specimens.

The method employed in the recent determinations is the following:—Weigh into a platinum crucible 1 grm. of the powdered sample, ignite, again weigh, then moisten with water, and add 2 or 3 c.c. of hydrofluoric acid, gradually heat to dryness, add about 7 grms. of sodium acid sulphate, gradually heat to low redness for one or two hours, cool, digest in 5 per cent diluted sulphuric acid for several hours, filter; to filtrate (method of A. Weller, *Ber. Deutsch. Chem. Gesell.*, xv., 2592), add about 1 c.c. of hydrogen peroxide solution and compare the colour so produced with one similarly obtained from a standard solution of titanic oxide.

To present a more satisfactory comparison with the amount of titanic oxide in the rocks, the percentage on the ignited soil is given together with that on the air-dried soil.

Nos. 1 to 12 are all from Albemarle Co., Va. 1 is dark

red clay, from Carter's mountain, farm of Rev. J. T. Randolph being the soil from which was formed a fulgite (?) which first drew my attention to this occurrence of titanic oxide. 2, deep red clay, one mile south of 1. 3, red clay, one mile north of 1. 4, red clay, one half mile west of 1. 5, light red sand, one mile north-west of 1. 6, red bottom soil, one and one half miles north-west of 1. 7, white micaceous soil, near McCormick Observatory, University Va., and three miles west of 1. 8, near chemical laboratory of University Va. 9, mica schist, one half mile north of 8. 10, deep red clay, ten miles south-west of 1. 11, red clay, ten miles west of 1. 12, Diorite, the rock which is most common in the above locality.

Nos. 13 to 17 are from other points in Virginia. No. 13 is deep red clay from farm of Mr. J. Shelton, Lowesville, Nelson Co. No. 14 a dark grey clay from swamp on Rappahannock River in Stafford Co. No. 15, a grey sandy loam, near Williamsburg, James City Co. No. 16, a yellow clay, per Mr. F. P. Brent, Onancock Creek, Accomac Co. No. 17, white sea-sand, from Virginia Beach, Princess Anne Co. The percentage of titanic oxide found in these respectively is as follows:—

Air-dried.	Air-dried.	Air-dried.	Ignited.
1. 5.42	7. 0.77	13. 1.87	
2. 1.45	8. 2.86	14. 0.88	
3. 2.73	9. 1.14	15. 0.49	0.50
4. 2.73	10. 1.86	16. 0.80	0.84
5. 0.33	11. 1.51	17. 0.07	0.07
6. 1.73	12. 1.15	Average 1.57	

Nos. 18 to 40 are from other portions of the United States. 18, a light brown loam, per Dr. A. C. Hopkins, Charlestown, W. Va. 19, a grey loam, per Mr. J. W. Rinehart, Foote, Mineral Co., W. Va. 20, pale red loam, a "limestone soil," per Mr. C. C. Councilman, Worthington's Valley, Baltimore Co., Md. 21, a grey yellow loam, per Dr. Simon Gage, Cornell University, N.Y. 22, a gritty yellow loam, per Dr. F. P. Venable, Chapel Hill, N.C. 23, a light yellow clay, one foot deep, per Mr. R. M. Cooper, near Black River, Sumter Co., S.C. 24, a grey clay, per Dr. P. S. Baker, over Carboniferous Limestone, Greencastle, Ind. 25, a grey clay, per Dr. W. A. Noyes, Terra Haute, Ind. 26, a deep orange clay sub-soil, per Prof. C. E. Wait, Knoxville, Tenn. 27, a pinkish china clay from a ten foot seam, and 28 a coarse grey clay from an eighteen foot seam, both per Mr. W. R. Searcy, Tuscaloosa, Ala. 29, a heavy grey clay, per Mr. A. P. Wright, river bottom soil, Bolivar Co., Miss. 30, light red surface loam, and 31 a grey sub-soil, both per Mr. Thos. Dunnington, Pine Bluff, Ark. 32, a brown clay, six feet deep, per Prof. W. H. Echols, Rolla, Mo. 33, a pale grey loam, per Dr. F. W. Traphagen, Deer Lodge, Montana. 34, a grey alkaline soil, from Truckee Valley, Nevada. 35, a yellow surface clay, per Dr. Masser, Los Angeles, Cal. 36, a brown clay, three feet deep, per Prof. H. E. Storrs, Los Angeles, Cal. Nos. 37 to 40 were sent by Prof. E. W. Hilgard, Berkeley, Cal. 37, upland red loam Station No. 1226, from Yuba River near Smartsville. 38, yellow grey Mesa soil, Station No. 1281, from Chino Ranch Station, San Bernardino Co. 39, "Red Mountain Land," Station No. 188, from a vineyard in Sonora Co. 40, a red loam, Station No. 1110, Thermolite Colony, Butte Co.

The percentage of titanic oxide found in these, respectively, is as follows (see Table next column).

Nos. 41 to 45 are from Oceania and Asia. Nos. 41 to 45 were sent by Prof. A. B. Lyons, Oahu College, Hawaii, Sandwich Islands. 41, a dark brown loam. 42 and 43, a yellow brown loam. 44, a brown clay. 45, a grey brown loam. 46, a light grey china clay, and 47 a grey china clay, both per Miss Mildred Page, Tokio, Japan. No. 48, a piece of a grey brick from the Great Wall of China, per Rev. Col-

* From the *American Journal of Science*, vol. xlii., Dec., 1891.
+ This acid was used before seeing the article of Dr. Noyes in *Journ. Anal. Chem.*, v., 39

* Dr. Noyes writes that he has recently found from 0.5 to 4 per cent of titanic oxide in a number of minerals from Arkansas.

Air-dried.	Ignited.	Air-dried.	Ignited.
18. 0.83	0.88	30. 0.52	0.62
19. 0.88	0.98	31. 0.60	0.62
20. 1.17	1.26	32. 0.57	0.65
21. 0.55	0.58	33. 0.44	0.50
22. 0.49	0.55	34. 0.57	—
23. 0.57	0.61	35. 0.72	0.82
24. 0.71	0.76	36. 0.49	0.53
25. 0.58	0.62	37. 0.77	0.85
26. 0.46	0.50	38. 0.72	0.75
27. 1.01	1.12	39. 4.93	6.05
28. 0.67	0.76	40. 0.90	0.97
29. 0.46	0.61	Average	0.85 0.98

lins Denny. 49, a pink clay, and 50 a yellow loam sub-soil from the bank of the Yellow River, and 51 a fine yellow silt from the old bank of the Yellow River. The three last specimens were sent by Dr. Edgar Woods, Tsing-Kiang-Pu, China. 52, light red pottery, from Kurrachee, Sind, India. 53, dark brown crucible clay, and 54 red furnace clay, both from Tumkur, India. The three last specimens were sent by H. B. M.'s Secretary for India. 55, grey loam from the shore of the Sea of Galilee, Palestine, per Rev. Collins Denny, of Vanderbilt University.

The percentage of titanic oxide found in these respectively is given below, and in making an average the specimens 41 to 45 are counted as one.

Air-dried.	Ignited.	Air-dried.	Ignited.
41. 4.43	5.25	49. 0.58	0.68
42. 2.40	3.37	50. 0.60	0.65
43. 2.25	3.11	51. 0.54	0.56
44. 4.00	4.64	52. 0.69	—
45. 2.78	3.37	53. 0.62	0.73
46. 0.70	0.80	54. 0.28	0.30
47. 0.40	0.50	55. 1.80 (?)	1.90
48. 0.55	0.55	Average	0.90 1.18

Nos. 56 to 72 are soils from Europe. Nos. 56 to 62 are from Russia, and were sent by Prof. Nich. Menschutkin, Kaiser University, St. Petersburg. 56 is a yellow sandy loam, "Souglinok," from Borovitsky, Novgorod. 57, dark grey loam, Prof. Docoutschaeff's type, "Solonetz" (barren black earth), Prilouky, Poltava. 58, brown grey loam, forest soil, Zenkovsky, Poltava. 59, dark grey loam, "Tschernosem" (black earth), Prilouky, Poltava. 60, sandy-black earth, "Tschernosem," Zenkovetsky, Polkava. 61, black earth, "Tschernosem," Balashoff, Saratoff. 62, black earth, "Tschernosem," Zeubrilovka, Saratoff. 63, white porcelain clay from Halle, Prussia. 64, white porcelain clay from St. Yrieux, near Limoges, France. 65, yellow grey loam from Florence, Italy, per Dr. C. L. Minor, of New York. Nos. 66 to 72 are from Great Britain, and were collected for me by Prof. W. G. Brown, of Lexington, Va. 66, black garden soil, Kensington, London. 67, dark grey loam from coast near Brighton. 68, grey loam, Liverpool. 69, grey sandy loam, Donnington, Lincolnshire. 70, grey sandy loam, Cambridge. 71, brown yellow clay, Inversnaid, Loch Lomond, Scotland. 72, brown clay under Forth Bridge, N. Queensferry.

The percentage of titanic oxide found in these, respectively, is as follows:—

Air-dried.	Ignited.	Air-dried.	Ignited.
56. 0.54	0.57	65. 0.53	0.62
57. 0.40	0.43	66. 0.21	0.27
58. 0.60	0.70	67. 0.46	0.52
59. 0.32	0.34	68. 0.41	0.46
60. 0.58	0.66	69. 0.45	0.49
61. 0.63	0.79	70. 0.50	0.53
62. 0.56	0.73	71. 0.85	0.89
63. 0.03	0.03	72. 2.36	2.52
64. 0.015	0.017	Average	0.54 0.62

This wide distribution of titanic oxide naturally suggests the examination of the rocks themselves. I have

so far been able to examine only the following typical rocks, the localities of which have furnished also the samples for analyses already published: 73, Trachyte, Kùhlsbrunnen; 74, Trachyte; 75, Trachyte, Drachenfels; 76, Hornblende andesite, Wolkenburg. These four were from the Siebengebirge. 77, Gabbro, Radauthal, Harzburg; 78, Melaphyr, Ilmenau, Schneidemüller-berg; 79, Melaphyr, Plauenschen Grunde, near Dresden; 80, Nosean phonolite, Castle Olbrück, Laacher See. These afford the following:—

	TiO ₂ mentioned in published analysis.	TiO ₂ found.
73. None	Zirkel, II., p. 181	0.22
74. "	" p. 182	0.86
75. 0.38	" p. 181	0.64
76. None	" p. 212	1.14
77. "	" p. 116	0.10
78. 0.89	" p. 55	1.01
79. Trace	Zirkel I., p. 584	0.36
80. None	"	0.18
	Average ..	0.56

While the frequent association of titanium with iron (as indicated by the colour after ignition) in these soils points to menaccanite as a source of the titanic oxide, yet the considerable amount of this substance in some of the clays and rocks containing little iron suggests that it may also result from titanite, which has been observed (Dana's "System of Mineralogy," p. 389) to be widely distributed in igneous rocks.

In conclusion, I desire to thank those who have assisted me in this work by supplying the desired specimens.

THE OXIDATION OF METALLIC ARSENIDES BY THE ELECTRIC CURRENT.*

By LEE K. FRANKEL.

(Concluded from p. 57).

Orpiment (As₂S₃).—The preliminary investigations made with this mineral showed that it came under the same category as the metallic arsenic. When the finely powdered mineral was introduced into the molten caustic potash, a volatilisation of the arsenic, recognisable by its odour, occurred. The precautions given under metallic arsenic regarding the cooling of the caustic potash and the regulation of the current were then introduced with successful results. Some difficulty may at first be experienced in obtaining correct control of the operation, but a few oxidations will give the operator sufficient experience to bring the decomposition to a successful completion. The conditions best adapted for the work are a current of 1 ampère, 25—30 grms. of caustic potash, the current being allowed to run for thirty minutes. Using these conditions, no arsenic was found in the slight residues which remained after decomposing the fusion, nor was any odour of arsenic perceptible during the entire course of the operation.

0.1443 gm. of orpiment decomposed according to the directions gave 0.1761 gm. of magnesium pyroarsenate = 59.08 per cent arsenic.

0.1044 gm. of orpiment yielded 0.12805 gm. magnesium pyroarsenate = 59.38 per cent arsenic.

0.2233 gm. of the same ore dissolved in nitric acid and weighed as magnesium pyroarsenate in a platinum crucible yielded 0.2755 gm. of magnesium pyroarsenate = 59.72 per cent arsenic.

Proustite (Ag₃AsS₃).—But a very small quantity of the mineral was available for analysis, and even that was intimately mixed with argentite. No attempt was there-

* I find in Bischoff, iii., p. 467, Gabbro from Rodanthal bei Steinbruch, contains TiO₂—1.75 per cent.

* Read at a meeting of the Chemical Section of the Franklin Institute, November 17, 1891.

fore made to extract the former mineral by hand-picking, but the entire mixture was placed in an agate mortar and ground, the grindings then being passed through a sieve. This removed all the proustite with some of the argentite, the greater portion of the latter remaining behind as flattened plates. Sufficient argentite, however, remained with the proustite to reduce in a considerable measure the percentage of the arsenic, and the deviation of the results from the theoretical percentage is attributable to this cause. Sufficient material was not at hand to make a check analysis by dissolving the mineral in nitric acid and determining in the usual way, but as the residues were most carefully examined for arsenic, and as none was found to be present, the natural conclusion arrived at was that the decomposition was complete. No loss of arsenic was noticeable during the entire operation, and the closeness of the results indicates that the decomposition of this mineral by the electric current can be accomplished as successfully as any one of those previously described. The conditions for oxidation were as follows:—A current of 1 ampère running for thirty minutes, the current being reversed during the last five minutes. The amount of caustic potash used was 25–30 grms. Below will be found the results obtained:—

1·1589 grm. of proustite weighed as magnesium pyroarsenate in a porcelain Gooch crucible gave 0·0147 grm. of magnesium pyroarsenate = 4·48 per cent arsenic.

0·2255 grm. of proustite yielded 0·0249 grm. of magnesium pyroarsenate = 5·34 per cent arsenic.

Besides these minerals already recorded several others were subjected to oxidation by the current, but owing to lack of material for the continuance of the work, satisfactory conclusions were not reached. The results are, however, of interest, and are, therefore, here appended.

Domeykite in Niccolite, $n(\text{Ni.As}) + m(\text{Cu}_2\text{As})$.—The mineral used for oxidation came from Michipicoten Island, and was a small section of a specimen in the mineral collection of the University of Pennsylvania, labelled whitneyite. Two oxidations of the mineral, in which the residues still showed arsenic, gave, to the surprise of the author, 35·3 per cent and 40·04 per cent of arsenic respectively, showing that the mineral could not be whitneyite, since this should contain theoretically 11·64 per cent of arsenic. A later oxidation gave, using 0·2207 grm. of the mineral, 0·2016 grm. of magnesium pyroarsenate = 44·22 per cent arsenic. 25–30 grms. of caustic potash were employed, with a current of 1 to 1½ ampères, for thirty minutes, reversing the current at the end for five minutes. In this oxidation no trace of arsenic was found in the residue. On reporting the results obtained to Dr. Koenig, he made an analysis of another sample by dissolving the mineral in nitric acid, and found it to contain 47 per cent of arsenic. This result is, however, not inharmonious with the last one obtained by the current, since, in a fresh fracture of the mineral, the niccolite and domeykite can be seen lying alongside of each other. Owing to this non-homogeneity, the sample analysed by Dr. Koenig may have contained more niccolite than the one used for oxidation by the current, and gave proportionately a higher percentage of arsenic. Unfortunately, the scarcity of the mineral necessitated the discontinuance of the work, and the question of complete oxidation is still in doubt. The few per cent difference in the results obtained by the two methods, however, indicates that the decomposition can be successfully accomplished under the conditions mentioned above.

Enargite ($3\text{Cu}_2\text{S.As}_2\text{S}_5$).—The material used for decomposition contained an admixture of gangue, and as with the domeykite, not sufficient of the substance was obtainable to settle thoroughly the question of oxidation. As the percentage of arsenic found, however, is within the neighbourhood of what the mineral ought to contain, and as no arsenic was detectable in the residue from the fusion, the result obtained is here appended without any definite statement regarding the thoroughness of the method. The amount of caustic potash used in the

oxidation was 25–30 grms., the current strength 1 ampère, with a reversal of the current at the end of the operation for five minutes. The arsenic was determined by weighing as magnesium pyroarsenate on a porcelain Gooch crucible.

0·2840 grm. of enargite gave 0·0770 grm. of magnesium pyroarsenate = 13·12 per cent arsenic.

The theoretical percentage of arsenic in the mineral is 19·1 per cent. If we remember, however, that the sample used contained gangue material, and that no arsenic was found in the residue, it is but fair to assume that the result lies within the limits of error, and that the oxidation is complete. No positive statement, however, can be made.

A study of the methods used for the determination of the arsenic in the various oxidations will be of interest. As has already been stated, the determination of the arsenic as arsenious sulphide by weighing on a porcelain Gooch crucible cannot be recommended owing to the great difficulty experienced in removing the sulphur with which the precipitate of arsenious sulphide is contaminated. The more common method of weighing the arsenic as magnesium pyroarsenate was found to be accurate if the conditions laid down for this determination are complied with, the method requiring at the same time great care. In the incineration of the filter from the magnesium ammonium arseniate constant vigilance was required to prevent a volatilisation of a portion of the arsenic, even though the filter had been previously saturated with a concentrated ammonium nitrate solution. And in many cases it was necessary to moisten the burnt filter several times with the solution before it could be completely reduced to ash. Weighing the precipitate on either a platinum or porcelain Gooch crucible removes these sources of error, and is, of all the methods so far mentioned, the most to be recommended. In the precipitations with magnesia solutions, it was noticed that the presence of large quantities of alkaline salts have a tendency to materially retard the precipitation of the magnesium ammonium arseniate, and it became necessary to allow the solution to stand at least forty-eight hours before the precipitation was complete. For this reason, where large quantities of alkaline salts are known to be present,—for example, the caustic potash used in the fusion,—it may be more advisable to reduce the arsenic with sulphurous acid, precipitate it as arsenious sulphide, filter and wash, and then re-convert it into arsenic acid and determine as magnesium pyroarsenate.

Owing to the time and care required in the above determinations, the method described in "Sutton's Volumetric Analysis," Sixth Edition, as recommended by Pearce, of the Colorado Smelting Company, was tried. The substance of the method is as follows:—"The arsenic brought into the form of alkaline arseniate is acidified with nitric acid, and boiled to remove carbon dioxide and nitrous fumes. It is then cooled to the ordinary temperature, and almost exactly neutralised as follows:—"Place a small piece of litmus paper in the liquid; it should show an acid reaction; now gradually add strong ammonia until the litmus turns blue, avoiding a great excess. Again make slightly acid with a drop or two of strong nitric acid, and by means of very dilute ammonia and nitric acid, added drop by drop, bring the solution to such a condition that the litmus paper, after having previously been reddened, will, in the course of half a minute, begin to show signs of alkalinity. The litmus paper may now be removed and washed, and the solution, if tolerably clear, is ready for the addition of silver nitrate. If the neutralisation has caused much of a precipitate (alumina, &c.), it is best to filter it off at once to render the subsequent filtration and washing of the arseniate of silver easier, "—." The latter portion of the process consists in determining the silver in the silver arseniate and calculating the percentage of arsenic from the amount of silver found.

A number of determinations were made by the author to ascertain the value of the method, but all of the attempts made resulted in failure. It was found well nigh impossible to tell by the colour of the litmus paper whether the solution was acid or alkaline. In several cases methyl orange was used as an indicator, and while the solution was made slightly alkaline, as recommended by Pearce, the addition of ammonia to the filtrates invariably brought down considerable quantities of silver arseniate, and the results obtained were proverbially low. The silver was not determined by titration, as recommended by Pearce, but by electrolysis. The best result obtained by this method, with the details of the operation, are given below.

A sample of rammelsbergite was decomposed under the conditions mentioned for that mineral. The fusion was decomposed with hot water, the insoluble material filtered off, and the clear filtrate acidified with nitric acid and boiled to remove the carbon dioxide. On cooling, ammonium hydroxide was added, the precipitated alumina, &c., filtered off, and the additions of dilute nitric acid and dilute ammonia made according to Pearce's direction, until the solution became faintly yellow, methyl orange having been used as an indicator. Silver nitrate was now added, the solution stirred, and the precipitate of silver arseniate filtered off. The addition of a drop of ammonium hydrate to the clear filtrate gave a further precipitation, and ammonia was therefore added until the precipitation was supposed to be complete. The two precipitates were then united, washed with cold water, dissolved in nitric acid, and the excess of acid evaporated. To the solution ammonium hydrate was added until the solution became alkaline, and then an excess of potassium cyanide, the solution electrolysed, and the resultant silver weighed. 64.21 per cent of arsenic was found, the same sample giving, by the pyroarsenate method, 70.34 per cent arsenic.

The author believes that with continued practice, sufficient dexterity might be obtained with the method to obtain accurate results, but it is hardly one that could be recommended for work outside of a technical laboratory, where absolute accuracy is not so essential a feature as that the results should be correct, relatively, to each other.

A comparison of the oxidation of the metallic sulphides with that of the metallic arsenides shows several points of difference. In the oxidation of the sulphides, it was observed by Dr. Smith that the process took place in three stages, the sulphur being first oxidised to hydrogen sulphide, then to sulphurous acid, and eventually to sulphuric acid. A similar state of affairs was not observed with the arsenides, and the oxidation evidently proceeds directly from metallic arsenide to arsenic acid. Even in samples where the oxidation had not been complete, and where the residues still showed undecomposed material, the filtrates from the fusion showed no trace of arsenious acid after the alkaline arseniate had been removed by precipitation with magnesia solution.

In conclusion, the author would here express his sense of deep obligation to Dr. Edgar F. Smith for his unremitting kindness during the progress of the above work, and for his constant help in assisting its completion.

Thanks are also due to Dr. George A. Koenig for samples of minerals, and to Mr. D. L. Wallace, of this laboratory, for assistance rendered in the oxidations.

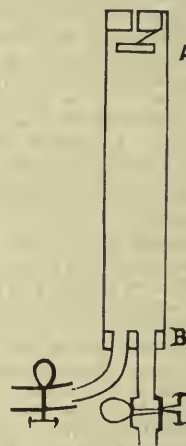
APPARATUS FOR MEASURING LIQUIDS QUICKLY.

By ALEX. F. REID, of Bonshaw, Stewarton, N.B.

SOME years ago I wrote an article (CHEM. NEWS, vol lvii., p. 39) on measuring liquids by drops. This was a somewhat slow method of measuring out liquids, except when

small quantities were taken. It is made use of very effectively by Dr. Bond, of Gloucester, in his acidometer for determining the acidity of milk, whey, &c. He uses a standard solution of caustic potash, with phenolphthalein as indicator. The milk or liquid to be tested is measured out in a piece of glass tubing up to a certain mark, and delivered into a small vessel. The caustic potash solution is dropped from a small dropping tube till the desired pink tint is produced, the number of drops corresponding to the degree of acidity.

The apparatus I am about to describe is on a larger scale. In some laboratories many solutions have to be measured out, and to do this quickly is much to be de-



sired. The following apparatus, which can easily be made, I find very serviceable in rapidly measuring out definite quantities of liquid:—

A piece of glass tube, A, B, is taken, and a cork is inserted in each end. Through the top cork a small hole is bored; this is closed on the under side by a valve of indiarubber cloth with a piece of cork attached to it. Through the bottom cork are bored two holes of about equal size, through which are passed two glass tubes. Two clips are attached to two pieces of indiarubber tube at the end of each of these glass tubes, as shown in the figure. The liquid is run into the apparatus through one of these tubes from a reservoir by opening the clip. The liquid rises up and lifts the piece of cork, thereby closing the valve. There is now the desired quantity of liquid in the apparatus, which can be run out by opening the other clip, the valve meanwhile falling down, as shown in the figure, ready to let the air escape in filling again.

The same apparatus makes a good burette if the tube A B is graduated and a little longer, as no time is lost in filling it to zero. It can thus be worked very quickly.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

UP to within the last year, the estimation of iron and aluminum in the presence of large quantities of phosphoric acid has always been attended with great difficulties, it being impossible to obtain results which approximated to the actual amounts of these bases present, or even agreed among themselves.

It was in connection with some analyses of phosphatic rocks in the work of the Chemical Division of the Department of Agriculture that my attention was first drawn to

* Read before the Washington Chemical Society, Nov. 12, 1891. From the *Journal of Analytical and Applied Chemistry*, Vol. v., No. 12.

this subject last spring, and I was directed by the chemist to make a thorough study of all the methods proposed for this work. In the following paper is found a *resumé* of the work I have done in this line. I will first give an abstract of the various methods which have been proposed.

The one which has been most generally used, and which is at the same time the most inaccurate, is conducted as follows:—

200 c.c. of a hydrochloric acid solution (=4 grms. material) are taken, and ammonia added to alkaline reaction. Care must be exercised not to add too great an excess, or time will be wasted in boiling it out. The ammonia precipitates the iron and aluminum together with the phosphoric acid. Boil the solution until the vapours are no longer ammoniacal. Allow the precipitate to settle, and decant the clear fluid on a filter. Wash with 50 c.c. of boiling water, stir, allow to settle, and decant as before. As some lime and magnesia may be carried down, dissolve in the beaker with as little hydrochloric acid as possible and re-precipitate with ammonia, boiling as before. Wash by decantation three or four times, using 50 c.c. of boiling water each time. Finally transfer to the filter with boiling water, wash free from chlorides, dry in air-bath at 110° C., ignite gently until the paper is burnt, then heat intensely, cool, and weigh.

The weight of phosphoric acid in this precipitate is found by any of the usual methods, preferably the molybdate method, and is deducted from the total weight, the oxides of iron and aluminum being thus found by difference.

Several methods have been elaborated which are based on the previous separation of the phosphoric acid. One of the first of these is that of Sonnenschein.

This method is applicable to all cases in which the phosphoric acid is present as orthophosphoric. The material is dissolved in dilute nitric acid and sufficient molybdenum solution added to precipitate all of the phosphoric acid. The precipitate of ammonium phosphomolybdate is filtered off and washed with a dilute solution of ammonium nitrate. A sufficient excess of ammonium sulphide is added to the filtrate, the molybdenum sulphide is removed by filtration, and the bases separated in the filtrate by means of ammonium hydrate.

This method should theoretically give correct and accurate results, but up to this time it has never been generally used, various analysts reporting their inability to obtain good results. The causes of the failure have never been satisfactorily explained.

Stutzer proposed the following method:—

Precipitate the iron and aluminum as phosphates by means of ammonia, collect on a filter, and wash once with water, then transfer filter and precipitate to a beaker and add 150 c.c. of molybdate solution to cause the separation of the phosphoric acid. Filter, and precipitate the bases in the filtrate by means of ammonium hydrate.

This method should also give good results, but it has been discarded, as in some inexplicable manner it would at times suddenly fail.

Dr. J. H. Vogel has investigated Stutzer's method very thoroughly, and takes the following exceptions to it:—That the addition of such a large amount of molybdate solution is not at all justified, and renders subsequent operations difficult, there being present 75 c.c. of concentrated nitric acid, which must be neutralised before the hydrates can be precipitated with ammonia. The presence of the filter also renders the washing of the precipitate difficult and necessitates a large amount of wash water. He has, therefore, modified the method as follows:—The precipitate of iron and aluminum phosphates is collected on a small filter. It is not washed, and in case the last drops of filtrate do not come through rapidly it is not necessary to wait, but the precipitate may be immediately dissolved, as small quantities of the filtrate do not change the results. The first precipitation of the phosphates by ammonia, according to Glaser (see description of this method), only serve the purpose of removing the bulk of

the phosphoric acid, as its presence would necessitate the use of very large quantities of the molybdate solution, and it is, on the other hand, necessary to work with small and concentrated amounts of the liquid. In all his experiments Dr. Vogel found that 50 c.c. of molybdate solution were sufficient. This amount, however, is regulated by the quantity of the precipitate which we have, and must be left to the judgment of the analyst. The 50 c.c. of the molybdate solution are put into a 100 c.c. graduated flask, and about 30 c.c. poured on the precipitate. The strong nitric acid present immediately dissolves the latter. The filter is then washed with the other 20 c.c., which have previously been diluted to 100 c.c. 100 c.c. are always sufficient for washing, and we need not consider any yellow colour present on the filter, as the acid wash water will rapidly remove all the bases. The filtrate and washings are allowed to stand until the phosphoric acid is completely precipitated. The whole liquid is then transferred to a filter and the beaker washed three or four times with a solution of ammonium nitrate, the filter being washed an equal number of times. The filtrate containing the bases is then rendered strongly alkaline with ammonia, and the liquid brought to the boiling-point. It is not necessary to expel the excess of ammonia, as the large amount of ammonia salts present prevents any solution of alumina or precipitation of magnesia. By proceeding in this manner we get a precipitate free from molybdic acid, unless we are working with very large amounts of iron and alumina, in which case the hydrates must be dissolved in dilute hydrochloric acid and reprecipitated with ammonia.

I now come to another modification of the molybdate method which I have used with perfect success, and which has invariably given accurate results both to me and to several other assistants in our laboratory. This modification was first used in this laboratory by Mr. K. P. McElroy, for the estimation of alumina in phosphatic baking powders.

100 c.c. (= 1 gm. substance) of a nitric acid solution of the substance are placed in a 500 c.c. flask, and a solution of ammonium molybdate added until all of the phosphoric acid has been precipitated. The addition of ammonium nitrate will hasten the separation of the ammonium phosphomolybdate. It is best to let the liquid stand over night. It is then made up to the mark, filtered through a dry filter, and duplicate samples of 200 c.c. each of the filtrate taken for analysis. A small quantity of ammonium nitrate is dissolved in the liquid and ammonia cautiously added, keeping the solution as cool as possible. The iron and aluminum will come down as hydrates. They are collected on a filter and washed with water, the filtrate and washings being collected in a beaker. It is usually best to re-dissolve the precipitate with a few c.c. of a solution of ammonium nitrate in dilute nitric acid, re-precipitate with ammonia, filter, wash, ignite, and weigh. This excludes all possibility of error by the presence of molybdic anhydride. After weighing, the oxides may be fused with sodium bisulphate, dissolved in water, and the iron determined volumetrically in the usual manner. My results on as small quantities of material as 0.200 gm. have always been closely concordant. I usually take four portions of 100 c.c. each (= 0.200 gm.); in two of these I determine both oxides gravimetrically, and in the other two I re-dissolve the freshly re-precipitated hydrates in dilute sulphuric acid and determine the iron volumetrically.

(To be continued.)

New Process for the Formation of Amidoalazarin.

—Charles Lauth.—The preparation of amidoalazarin β is generally effected by the reduction of nitroalazarin either by means of hydrogen sulphide and ammonia or by means of glucose in presence of sulphuric acid or by means of zinc and potassa. The reduction can be effected as well and very easily by the action of dimethylaniline.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 22nd, 1892.

Prof. O. J. LODGE, F.R.S., Vice-President, in the Chair.

MESSRS. J. B. Peace and E. G. Highfield were elected members of the Society.

Prof. G. F. FITZGERALD, F.R.S., read a paper "*On the Driving of Electromagnetic Vibrations by Electromagnetic and Electrostatic Engines.*"

The author pointed out that as the electromagnetic vibrations set up by Leyden jar or condenser discharges die out very rapidly, it was very desirable to obtain some means whereby the vibrations could be maintained continuously. Comparing such vibrations with those of sound he said the jar discharges were analogous to the transient sound produced by suddenly taking a cork out of a bottle; what was now required was to obtain a continuous electromagnetic vibration analogous to the sound produced by blowing across the top of a bottle neck. In other words some form of electric whistle or organ-pipe was required.

These considerations led him to try whether electromagnetic vibrations could be maintained by using a discharging circuit, part of which was divided into two branches, and placing between these branches a secondary circuit tuned to respond to the primary discharge. This did not prove successful on account of there being nothing analogous to the eddies produced near an organ pipe slit. The analogy could, he thought, be made more complete by utilising the magnetic force of the secondary to divert the primary current, first into one of the two branches and then into the other.

If spark gaps be put between two adjacent ends of the branches and the main wire, then the magnetic effect of the secondary current should cause the spark to take the two possible paths alternately. Electrically driven tuning forks and vibrating spirals were cases in which magnetic forces set up vibrations, but here the frequency depended on the properties of matter and not on electrical resonance. The frequency of delicate reeds could, however, be controlled by resonance cavities with which they were connected, and he saw no reason why the same action could not be imitated electromagnetically, using an electric spark as the reed.

Referring to the properties of iron in connection with electromagnetic vibrations, he pointed out that a prism of steel 1 m.m. long had a period of longitudinal vibration of about one-millionth of a second, and as this was comparable with the rates of electromagnetic vibrations, the immense damping effect which iron had on such vibrations might be due to the setting up of sound vibrations in the material.

Other methods of driving electromagnetic vibrations had suggested themselves in the shape of series dynamos or alternators. The polarity of a series dynamo driving a magneto motor would, under certain circumstances, reverse periodically, and thus set up an oscillatory current in the circuit. Similar effects can be got from series dynamos charging cells or condensers. In an experiment made two weeks before with Planté cells and a gramme dynamo, reversals occurred every fifteen seconds.

Greater frequencies might be expected with condensers. The latter case he had worked out theoretically. He had also tried experiments with Leyden jars and a dynamo, but got no result. This might have been expected, for the calculated frequency was such as would prevent the currents and the magnetism penetrating more than skin deep.

Calling the quantity of electricity on the condenser Q , the differential equation for a dynamo of inductance L , and resistance r , and a condenser of capacity X is—

$$L \ddot{Q} + r \dot{Q} + \frac{Q}{X} = \dot{L} \dot{Q}$$

or—

$$L \ddot{Q} + (r - \dot{L}) \dot{Q} + \frac{R}{X} = 0.$$

If L be = 0 the solution of the equation is—

$$Q = Q_0 \epsilon^{-\frac{r}{L} t} \cos. 2\pi \frac{t}{T},$$

and the rate of degradation of amplitude depends on the factor—

$$\epsilon^{-\frac{r}{L} t}.$$

If, however, L be greater than r , the exponent of ϵ becomes +, and hence Q would go on increasing until limited by the saturation of the iron or the increased resistance of the conductors due to heating.

A dynamo without iron, provided one could be made to run fast enough to send a current through itself, would be likely to give the desired effect. The author thought that by making such a dynamo large enough, and its armature very long, it would be possible to get a frequency of about one million.

Electrostatic machines seem, however, to be more promising driving agents. Like series dynamos their polarity depends on the initial charge, and can be easily reversed. Hitherto such machines have been inefficient, mainly on account of the sparking in them, but Maxwell had shown how this could be obviated. There was the same kind of difference between electromagnetic and electrostatic machines as between Hero's engine and the modern pressure engine. Like modern engines, electrostatic machines worked by varying capacity, but the effect of this variation in electrostatic machines was only to vary the frequency and not the rate of degradation.

From the fact that electrostatic multipliers could be driven by alternating currents, he thought they might be made to drive alternating currents. If magnetic currents could be obtained then electrostatic engines would easily be produced.

In conclusion, the author described a modified electrostatic multiplier which he believed offered a feasible solution of the problem. In this machine the collectors were supposed joined to the ends of the vibrating circuit and would, therefore, become + and - alternately. Inductors and brushes were to be so arranged that an insulating cylinder turning between them should have many + and - charges distributed alternately round its periphery. By suitable adjustment these charges could be collected at the proper instants so as to keep up the vibration.

The Chairman, Prof. LODGE, said the paper was very suggestive and full of interesting points.

The subject of electromagnetic vibrations was attracting great attention in America in connection with the Manufacture of Light. Hertz oscillations die out too soon to be satisfactory, for their duration rarely exceeds a thousandth part of the interval between consecutive discharges.

The theory of dynamos charging condensers he considered extremely interesting, and thought the fact that the damping factor could be changed in sign must have tremendous consequences.

Dr. W. E. SUMPNER asked a question about a method of doubling frequency of alternation recently described by Mr. Trouton, in which the armature of one alternator excites the fields of a similar machine. Mr. Trouton had said that after once doubling the frequency it was not possible to go on doing so. He (Dr. Sumpner) thought that by adding other machines the frequency could be still further increased, and gave a proof of the fact.

In reply, Prof. FITZGERALD said that adding another machine increased the frequency by a given amount, and

did not double the preceding one. Hence, to increase the frequency a thousandfold a thousand machines would be required, and on this account Mr. Trouton considered it impracticable.

Prof. S. P. THOMPSON thought the paper very suggestive, and the acoustic analogies very interesting. Melde's apparatus was an instance of doubling or halving a frequency. On reading the title of the paper he had expected hearing of a method of maintaining electromagnetic vibrations by giving occasional impulses in some such way as that in which a tuning fork could be kept vibrating by allowing the hammer of a trembling bell to knock against. There was another method of intensifying electric oscillations which he had seen mentioned in a Patent Specification by Sir W. Siemens, who suggested using a series dynamo with a telegraph cable to augment the signalling currents.

On the subject of ironless dynamos he (Prof. Thompson) desired further information. Some years ago he had made calculations and found the speed at which they would require to run was so enormous as to be beyond the range of engineering possibility.

Mr. C. V. BOYS, referring to the author's suggestion of using an electric spark with alternate paths to maintain vibration, said that he had tried whether an oscillatory spark was displaced by a magnetic field, but the displacement even when photographed by a revolving mirror was barely appreciable.

Prof. PERRY asked for an explanation of the term "skin deep magnetism." He was not previously aware that Sir W. Siemens had described a method of improving cable signalling by using a series dynamo. He himself had patented a somewhat similar arrangement. He had also made a dynamo without iron, but had not got it to work.

In reply to Prof. Perry the author of the paper said that in electromagnetic vibrations the magnetic force alternates so rapidly that it could not penetrate far into the field magnet of a dynamo before it is reversed; hence the magnetism would only be skin deep.

Dr. BURTON suggested that a commutator with many segments, something like that used by Mr. Gordon in his "Researches on Specific Inductive Capacity," might possibly be employed for producing high frequencies.

A communication on "Supplementary Colours," by Prof. S. P. THOMPSON, F.R.S., was postponed.

ROYAL INSTITUTION OF GREAT BRITAIN.

Special General Meeting, Monday, February 1, 1892.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following Address to Her Majesty the Queen, Patron, and His Royal Highness the Prince of Wales, Vice-Patron of the Royal Institution, in reference to the decease of His Royal Highness the Duke of Clarence and Avondale, Honorary Member of the Institution, was read and unanimously adopted:—

"The Members of the Royal Institution of Great Britain, in Special General Meeting here assembled, desire most respectfully to offer to Her Majesty the Queen (Patron of the Royal Institution) and the Prince of Wales (Vice-Patron of the Institution) the expression of their unfeigned sorrow at the loss which Her Majesty, His Royal Highness, and the Nation have sustained by the death of His Royal Highness the Duke of Clarence and Avondale (Honorary Member of the Institution), and they ask to be allowed to tender their heartfelt sympathy and condolence with Her Majesty and His Royal Highness the Prince of Wales in their bereavement."

Letters of regret for non-attendance were read from His Grace the President, the Earls of Derby and Ducie, Sir John Fowler, and many others.

NOTICES OF BOOKS.

Manual of Chemical Technology. By RUDOLF VON WAGNER. Translated and Edited by WILLIAM CROOKES, F.R.S., Past Pres. C.S., and Pres. Institute Electrical Engineers. From the Thirteenth enlarged German Edition, as Remodelled by Dr. FERDINAND FISCHER. With 596 Illustrations. London: J. and A. Churchill, 1892. Large 8vo., pp. 968.

THE value of this capital work has been most fully recognised, since its thirteenth German edition has already appeared. In accordance with the rapid advance and improvement in the chemical arts, alterations, omissions, and additions have been largely necessitated; a task which has been most ably performed by Dr. F. Fischer. In consequence, the English version of 1872 has to a great extent been superseded, and possesses mainly a historical value. During the last twenty years, new materials have been introduced into commerce, new processes devised, and former materials discarded, as most strikingly exemplified in the tinctorial trades and in the manufacture of colours. One of the chief improvements in the latest German edition, and, of course, in the English version now before us, is a re-arrangement of the subject. Dr. Fischer, in the spirit of the old name given to chemists, "philosophers by fire," gives the first place to fuel, and argues that more intelligent care shall be turned to its utilisation. The interests of the world demand that every pound of coal should be made to yield its utmost share of duty. Hence, we cannot help confessing that England has been, and still is, the foremost transgressor; because we have used it recklessly, wasting in our domestic fires certainly not less than 90 per cent of the heat producible, and generating smoke to a fearful extent. Our readers will remember the solemn execration pronounced upon us by Liebig for the waste of our sewage matter—a crime still committed by all those who either run the sewage direct into the sea, or who precipitate it and then carry it out to sea in barges. But it appears to us that we have equally deserved a similar anathema for our treatment of coal. Dr. Fischer contends in the work before us that "hundreds of thousands of stoves in Germany which have imperfect doors or none at all, allow from 50 to 80 per cent of the entire combustion value of the fuel to pass up the chimney." He is of opinion that no substitute for coal can be thought of.

A peculiarity of this edition are the illustrations, which are excellent, and the lettering for reference is perfectly clear.

A verbatim translation of the original has been in many parts impossible. Passages which refer to conditions existing only in Germany have been, of course, omitted.

The work before us is remarkably comprehensive. It gives an able, accurate, and intelligent survey of the entire extent of chemical industry, with the singular exception of quinine, morphine, and the other medical alkaloids.

As an instance of the different manners in which the laws of Germany and of England respectively interfere with chemical manufactures, we may refer to alcohol. In Germany, spirits for technical (or scientific) purposes are exempt from taxation if they are "denaturalised by any one of a variety of methods which the manufacturer may select." The most suitable of all these agents is Dippel's animal oil. In Germany, we see that the Revenue Authorities are not allowed to ride rough shod over the interests of science and manufactures in the manner which is tolerated in "free" England.

The reader may at first sight feel surprised at finding milk, meat, &c., discussed in a work like the present; but, though these substances are certainly natural products, yet their preservation depends on chemical principles. Prof. Neubauer's protest against artificial wine as here quoted from his celebrated "Chemie des Weines"

deserves to be widely known. He justly denounces it as "elandes Machwork"—a miserable counterfeit.

The main sections of the work treat of the technology of fuel, including lighting gas, the production of light, photometry, and the electric light; metallurgy in its widest sense; chemical manufacturing industry, including water, its examination, purification, and industrial applications; and thermo-chemistry—a subject which the industrialist can no longer safely overlook, since he may by its means learn if any proposed process is practicable or not. A peculiar interest attaches, of course, to the manufacture of soda and its by-products, which is now in a state of transition.

Section IV. treats of the organic chemical manufactures.

The chapters here devoted to the artificial colouring-matters and their examination are excellent, and go into practical details more than might be expected in work of such general scope.

The fifth section takes up glass, earthenware, cements, and mortars.

In the sixth we have an account of articles of food and consumption. The author's conclusions on the nutritive value of different kinds of food are instructive, though we fear the vegetarians will not be edified by learning that "meat, eggs, and milk are most completely utilised; vegetables much less thoroughly, as from 20 to 40 per cent are excreted undigested. A powerful body can scarcely be built up and maintained on a purely vegetable diet."

In the seventh section, we have the chemical treatment of fibres, including their cleansing, recognition, bleaching, dyeing, and printing; the manufacture of paper being naturally appended.

The last section is occupied with a somewhat promiscuous assortment of organic chemical arts and manufactures, tanning, glue, bone-black, fatty matters, soaps, stearine, and glycerin; the essential oils and resins; and the preservation of wood.

The editorial foot-notes in this edition are a most valuable feature. Many of them supply important facts overlooked in the original or discovered subsequently to the appearance of the last German edition. Very many are bibliographical, referring the reader to special works in which various subjects are treated more in detail than would have been possible in the work before us.

We are of opinion, however, that a treatise like the present, which gives a fair and accurate survey of the whole extent of chemical industry, is indispensable. With reference to the many special treatises which have lately appeared, it plays a part like that taken by a "key-map" in relation to the maps of provinces and cities. The various chemical arts throw cross-lights upon each other, often when least expected. Hence, to the rational industrialist, no less than to the student, this work will be invaluable.

Chemistry of the Carbon Compounds, or Organic Chemistry.

By Prof. VON RICHTER, of the University of Breslau. Authorised translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Second American Edition from the Sixth German Edition, with Illustrations. London: Kegan Paul, Trench, Trübner, and Co., Limited, 1891. 8vo., pp. 1040.

THIS book, though, according to its title page, it is published in London, has been written and printed in the United States, as may easily be seen from its peculiar orthography, and from a few expressions which are unusual on the eastern side of the Atlantic. The multitude of students, or, at least, of intending examinees, who busy themselves with chemistry, is an admitted fact. Still, the outsider is puzzled to account for the number of general chemical manuals of all sizes which are continually issuing from the press. How these works, the subject-matter of which is practically identical, find publishers is remarkable in times where original scientific

productions meet with little acceptance, and is a question which has not yet found its *Oedipus*. Not content with the hand-books and manualettes of native origin we introduce English versions of German and French treatises, and now it seems American editions are making their appearance. All this is done in the absence of any discovery calculated to open up a new epoch in the history of Science. That the work before us is fully on a level with the present state of chemistry, that its views are correct, and its arrangement perspicuous, the name of Prof. von Richter is a full guarantee. No compound of importance is omitted, and although the descriptions are necessarily condensed they are accurate.

After an introduction, in which the general principles of organic chemistry are laid down, the two great classes of the fatty and the aromatic compounds and of the benzene—or as they are more commonly called aromatic—bodies are described. Lastly come certain compounds such as the alkaloids, the terpenes, the resins, &c., the constitutions of which have not yet been satisfactorily ascertained.

One feature is particularly satisfactory. The translator, not having the fear of any examiner before his eyes, has reproduced the work as he found it, without any alterations or additions supposed to be needful according to the requirements of the English or American student. There is no reference to preparing for any examination.

Experiments in General Chemistry. Systematically and progressively arranged. By LYMAN C. NEWELL, A.M., Instructor in Physical Science, High School, Pawtucket, Rhode Island. Pawtucket: Sibley and Lee.

WE have here a pamphlet of 23 pp. describing experiments to be made upon some thirty of the elements. The author gives the opinion that a careful performance of each experiment may not make a chemist, but it will make a sound thinker, and "to think is to live." This dictum is not unquestionable. Sometimes to think is to die. We notice the proviso as concerning the ignition of a mixture of hydrogen and air, "*perform this experiment with care.*" But will a *tyro*, perhaps without the presence of a teacher, know what kind of care is meant.

Elsewhere we read, anent the action of bleaching powder upon coloured tissues, "the chlorine destroys the organic matter in the cloth." Would it not be more accurate to say "destroys the colouring-matter in the cloth?"

Under hydrochloric acid the pupil is told to "cautiously touch a drop to the tongue;" and how is he to know the kind and amount of caution necessary? We think *with* the tongue would be a better expression. Several other passages in the pamphlet would be more intelligible if differently worded.

CORRESPONDENCE.

PAYMENT BY RESULTS.

To the Editor of the Chemical News.

SIR,—“Let it be granted that all teachers are thieves,” postulated Parliament, and proceeded to elaborate a system whereby a thief might be set to catch a thief.

The effect of the system has been only too apparent to those who are capable of thinking straight and seeing clear, and Professor Humboldt Sexton has once more attempted to draw public attention to it in your issue of Jan. 15. But the public are past help in their blindness, for they *will* not see.

The result of regarding every teacher as a thief has been to compel him to become one. For what else can be said of him who sets aside all conscientious scruples

as to the utility of what he is teaching and the progress of his pupil, and converts himself into a machine for obtaining as much money from the public as the brains put under his charge will enable him to obtain? Yet such a course is the only alternative to starvation for him.

Now, Sir, there are at present being established in London several Institutions which are called and are to be called "Technical Institutes." These are supposed to be intended for the education of craftsmen in such sciences as may underlie the technique of their crafts—technical education no doubt expresses this, but has, unfortunately, become a shibboleth meaningless to many.

I submit, Sir, that these Institutions will one and all miss their mark if they be suffered to associate themselves with "the Department;" their teachers will at once be branded as thieves; and, lest they earn not enough grants for their employers, will neglect the unpromising craftsman for the smug board-school teacher, thus converting the so-called Technical Institutes into so many more night schools, of which there are at present plenty that turn out excellent "passes."—I am, &c.,

"ONE OF THE THIEVES."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

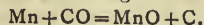
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 3, January 18, 1892.

Organic Compounds as Solvents of Salts.—A. Etard.—If the lines of the solubility of salts in water are beginning to be fairly well known it is not the same with other solvents. In a few cases a point of saline solubility in alcohol or ether has been determined, but the general progress of the phenomenon as a function of temperature still remains unknown for the various liquid media. Water, on account of its chemical and physical properties, is an exceptional solvent. It cannot be compared with any other, since it combines in various proportions with the majority of salts whilst still playing the part of a solvent. This double action renders the conclusions drawn from experiments very doubtful. The organic liquids rarely combine with salts. The anhydrous mercuric and cupric chlorides have, however, allowed of measurements which are summarised graphically in a subjoined table. Water dissolves sublimate between 0° and 120° along a curve, and from this temperature up to 150° the points lie in a right line. The experiments cannot be pushed very far above 150°, the salt is dissociated and chlorine is liberated in the liquid. The solutions, which up to 120° deposit on cooling the well-known needles of anhydrous mercuric chloride give above this temperature white nacreous tablets resembling in form mercuric iodide. Absolute methylic alcohol approaches very near to water. It is water in which a hydrogen has been replaced by a carbide radicle very near to CH₃. Absolute ethylic alcohol presents a double perturbation between -50° and +60°. In the organic liquids, as in water, mercuric chloride is deposited from hot solutions in tablets. Both with the organic liquids and with water we may observe right lines of solubility directed towards its fusion point. This fact, the demonstration of which the author intends to pursue, will establish for salts a direct connection between the gaseous state and the state of solution.

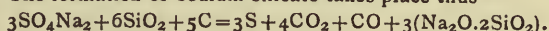
Action of Carbon Monoxide upon Iron and Manganese.—M. Guntz.—In the author's experiments it appeared that at dark redness iron seemed to absorb carbon monoxide, whilst it was blackened by a deposit of carbon; carbonic acid was also evolved, though in small quantities. Pure manganese absorbed the carbon mon-

oxide, producing even a partial vacuum in the apparatus. This gas is dissolved according to the formula—



At very high temperatures manganous and ferrous oxides, if heated with carbon, yield metal and carbon monoxide, the inverse reaction of that which takes place about 500°.

Action of Carbon upon Sodium Sulphate in Presence of Silica.—Scheurer Kestner.—It is generally admitted that the reactions effected between the alkaline sulphates, carbon, and silica, in the production of glass or of soluble silicates, are represented by the equation $2\text{RSO}_4 + \text{C} = 2\text{SO}_2 + \text{CO}_2 + 2\text{RO}$. If the proportion of carbon is insufficient the glass is incomplete and contains an alkaline sulphate; if it is too large the glass is sulphurous, and its solution, in case of sodium silicate, blackens lead salts. But the necessary quantity of carbon considerably exceeds that which answers to the above equation. From the author's experiments he concludes that the sulphur of the sodium sulphate is entirely given off as a vapour mixed with much carbon dioxide and a smaller quantity of carbon monoxide. Even in presence of a large excess of sulphate the proportion of carbon monoxide remains important, and forms the sixth part by volume of the total gas produced. It is probable that this carbon monoxide is derived from a decomposition giving rise to sulphurous acid, which is in turn decomposed at higher temperatures by the carbon. The formation of sodium silicate takes place thus—



On a Lithium Nitride.—L. Ourard.—Lithium heated in a current of nitrogen contained:—

Lithium (total)	54.18
Nitrogen	35.86
Silica	6.84
Oxygen	3.12

100.00

Of the lithium 2.73 was combined with oxygen and 51.45 with nitrogen. The compound produced seems to be NLi₃.

Action of Phosphorus Perchloride upon Ethyl Oxalate.—A. Feuconnier.—By the reaction of the two constituents the author obtains oxalyl chloride, and on heating 2 mols. phosphorus perchloride and 1 mol. ethyl oxalate, he produces a mixture of ethyl and oxalyl chlorides and phosphorus oxychloride. Oxalyl chloride is a colourless, mobile liquid, fuming strongly in the air. It is decomposed in contact with water, yielding oxalic acid.

The Value of the Two Functions of Glycol.—M. de Forcrand.—Not adapted for useful abridgment.

An Isomer of Camphor.—Ph. Barbeir.—This new isomer of camphor, to which the author gives the name puleone, exists in the essential oil of *Mentha pulegium*. Its composition is C₁₀H₁₆O. It is colourless, very mobile, with a strong odour of mint; it is insoluble in water, soluble in alcohol, ether, and benzene. It boils at 222°–223°. Its specific gravities at 0° and 23° are 0.9482 and 0.9293. It is dextrorotatory, and its rotatory power for the ray D is [α]_D = -25.15°. The indices of refraction with relation to two rays of tin are—

$n_r = 1.4833$	$n_f = 645$
$n_b = 1.4997$	$n_b = 452.6$

Puleone contains the functional group of the ketones. It does not contain ethylenic groups.

Fixation of Iodine by Starch.—E. Rouvier.—There is formed in presence of an excess of starch a compound different from that formed in presence of an excess of iodide.

Action of Boric Acid upon Germination.—J. Moret.—It may be concluded that boric acid in solution, if placed in contact with the seeds of plants, retards and even prevents germination if the contact is sufficiently

prolonged. Boric acid will probably act strongly upon the lower fungi and kindred organisms. If this is the case boric acid may be employed in combating mildew, *anthracnose*, *oidium*, &c.

Rotatory Power of Silks of Different Origin.—Leo Vignon.—The molecular rotatory powers measured have all the same sign. For the gum they are comprised between -30° and -45° , and for the fibroines between -39.5° and -48.2° .

Sodium Chloride in Plants.—Pierre Lesage.—On watering *Lepidium sativum* and *Raphanus sativus* with dilute sea-water or dilute brine, we find in the plants the elements of this salt, which are therefore absorbed in a certain proportion.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. vi., No. 11.

The Conditions which should be Presented by Fermentable Solutions in order that Fluorides may Produce in them a Maximum Effect.—J. Effront.—The experiments recently undertaken by the author prove that the beneficial action of the fluorides depends on a number of conditions. The acidity of the wort especially regulates the antiseptic action; in a neutral wort it is nearly null, but increases with the acidity. The acidity plays a very important part in the special action of the fluorides upon the protoplasm of the cellules, but the presence or absence of phosphates constitutes one of the most important conditions of the activity of the phosphates.

Preparation of Zinc-Hydroxylamine.—L. Crismer.—On account of a memoir recently published by M. Lobry de Bruyn, the author is compelled to make known two very simple procedures for the preparation of crystalline hydroxylamine, which depend on the use of the zinc salt.

Preparation of Crotonic Aldehyd.—A. Müller.—The best yield is obtained by heating for forty-eight hours 100 grms. of absolute ethylic aldehyd with 0.7 c.c. of a solution of zinc chloride containing 150 grms. of this salt in 100 c.c.

The Presence of an Aldehyd with Four Atoms of Carbon in a Piquette Brandy.—J. A. Müller.—The author finds it remarkable to meet in a brandy with a relatively considerable quantity of an aldehyd having a definite composition.

Action of Sulphur upon Metallic Solutions.—J. B. Senderens.—The author describes first the action of sulphur upon the alkaline and alkaline-earthly bases; next the action of sulphur upon the metallic oxides in presence of water; thirdly, the action of sulphur upon salts in presence of water, taking in succession the sulphates, nitrates, and chlorides, the acetates, the carbonates, the silicates, including glass and various polybasic salts. He treats lastly of the action of sulphur upon water. He maintains that under these conditions the production of hydrogen sulphide affirmed by De Gerard, denied by Gélis, and re-affirmed by Cross and Higgin, is very slight.

Action of Light upon Silver Chloride.—A. Béchamp.—Already noticed.

MISCELLANEOUS.

Royal Institution.—Professor E. Ray Lankester, F.R.S., will, on Thursday next, February 11, begin a Course of three Lectures on "Recent Biological Discoveries"; and the Right Hon. Lord Rayleigh, F.R.S., will, on Saturday, February 13, begin a Course of six Lectures on "Matter, at Rest and in Motion."

The Royal Society of New South Wales.—Original Researches.—The Royal Society of New South Wales offers its Medal and £25 for the best communication (provided it be of sufficient merit) containing the results of original research or observation upon each of the following subjects:—

Series XI.—To be sent in not later than May 1, 1892.—No. 37. On the Iron Ore Deposits of New South Wales; 38. On the Effect which Settlement in Australia has produced upon Indigenous Vegetation, especially the depasturing of sheep and cattle; 39. On the Coals and Coal Measures of Australasia.

Series XII.—To be sent in not later than May 1, 1893.—No. 40. Upon the Weapons, Utensils, and Manufactures of the Aborigines of Australia and Tasmania; 41. On the Effect of the Australian Climate upon the Physical Development of the Australian-born Population; 42. On the Injuries occasioned by Insect Pests upon Introduced Trees.

Series XIII.—To be sent in not later than May 1, 1894.—No. 43. On the Timbers of New South Wales, with special reference to their fitness for use in construction, manufactures, and other similar purposes; 44. On the Raised Sea-beaches and Kitchen Middens on the Coast of New South Wales; 45. On the Aboriginal Rock Carvings and Paintings in New South Wales.

The competition is in no way confined to Members of the Society, nor to residents in Australia, but is open to all without any restriction whatever, excepting that a Prize will not be awarded to a Member of the Council for the time being; neither will an award be made for a mere compilation, however meritorious in its way. The communication, to be successful, must be either wholly or in part the result of original observation or research on the part of the contributor. The Society is fully sensible that the money value of the Prize will not repay an investigator for the expenditure of his time and labour, but it is hoped that the honour will be regarded as a sufficient inducement and reward. The successful papers will be published in the Society's annual volume. Fifty reprint copies will be furnished to the author free of expense. Competitors are requested to write upon foolscap paper—on one side only. A motto must be used instead of the writer's name, and each paper must be accompanied by a sealed envelope bearing the motto outside, and containing the writer's name and address inside. All communications, to be addressed to the Honorary Secretaries, F. B. KYNGDON and W. H. WARREN, The Society's House, Elizabeth Street, Sydney.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.**—Medical, 8.30.
— Society of Arts, 8. "Developments of Electrical Distribution," by Prof. George Forbes, F.R.S.
- TUESDAY, 9th.**—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8. (Anniversary).
- WEDNESDAY, 10th.**—Society of Arts, 8. "Burning Oils for Light-houses and Lightships," by E. Price Edwards.
— Geological, 8.
— Pharmaceutical, 8.
- THURSDAY, 11th.**—Royal, 4.30.
— Royal Institution, 3. "Some Recent Biological Discoveries," by Prof. E. Ray Lankester, M.A.
— Society of Arts, 4.30. "Recent Travels in Indo-China," by Lord Lamington.
— Institute of Electrical Engineers, 8.
— Mathematical, 8.
- FRIDAY, 12th.**—Royal Institution, 9. "On Rain, Snow, and Hail," by G. J. Symons, F.R.S.
— Astronomical, 3. (Anniversary).
— Physical, 5.
- SATURDAY, 13th.**—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

TO CORRESPONDENTS.

E. Toray.—As you put it we do not see how it is possible.

THE CHEMICAL NEWS.

VOL. LXV., No. 1681.

THE ALDE-ACIDS.

By J. ALFRED WANKLYN and WILLIAM JOHNSON.

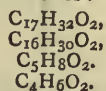
Valerianic Acid.—There are four possible valerianic acids, viz., the normal acid and three iso-acids; and, consequently, there are three possible alde-valerianic acids. There is an acid which has been known to chemists for forty years under the name of angelic acid, $C_5H_8O_2$. It is a crystalline solid, fusing at $45^{\circ}6'$, and volatile, boiling at $190^{\circ}6'$. We expect to find that this acid is one of the four possible alde-valerianic acids, and we call attention to the fact recorded in "Watts's Dictionary," that valerianic acid when oxidised by alkaline permanganate yields a crystalline acid, supposed to be angelic acid.

We have operated upon commercial valerianic acid with alkaline permanganate and obtained a crystalline acid which we intend to investigate.

Ascending the series, we have experimented upon palmitic acid and margaric acid. The specimen of palmitic acid was prepared from palm oil and carefully and laboriously purified. Its baryta salt was found to contain 20.92 per cent of barium. Some of this was oxidised by alkaline permanganate and converted into a different acid, which furnished a baryta salt containing 21.31 per cent of barium. Theory for alde-palmitate of baryta—barium 21.31 per cent.

The margaric acid was that which in commerce passes under the name of stearic acid. Operating upon this acid we have shown that when gently heated in the water-bath in presence of alkaline permanganate and much water, it is attacked and converted into a new acid possessing very marked properties. There appears to be no—or next to no—utter destruction. In our experiment, 2.34 grms. $C_{17}H_{34}O_2$ reduced 0.880 gm. $KMnO_4$ to the state of H_2OMnO_2 , and yielded 2.25 grms. of the new alde-margaric acid; the formula of which we expect will be $C_{17}H_{32}O_2$.

We are engaged in an extended investigation of the new acids and believe we have in our hands the following members of the alde-acid series:—



There is a strong family likeness running through them, and some of them are destined to become important in many ways.

ON THE EXPLOSION OF SODIUM BOTTLES.

By Dr. T. L. PHIPSON, F.C.S., &c.

A RECENT number of the CHEMICAL NEWS (vol. lxx., p. 61) contains a letter from Mr. A. Merry, of Swansea, which gives an account of the explosion of a bottle containing sodium which had stood unused in a laboratory for two years, the petroleum which covered the metal having, it is supposed, been evaporated so as to leave the metal in contact with the air. The writer of the letter demands an explanation of the phenomenon.

I have two bottles of sodium prepared by Henri Ste.-Claire Deville, in Paris, about the year 1858. I brought them to London with me in 1860, and they have thus been for upwards of thirty years on the shelves of my laboratory. They are stoppered glass bottles. One of them has been

frequently opened, and its supply of sodium is now reduced to about one-quarter of what it originally was. The other has been used less frequently and is still nearly full. From time to time the petroleum which covers the metal has been added to, in order to supply the loss that occurs by slow evaporation, in spite of the excellent glass stoppers. But of late years this evaporation by the stoppers has entirely ceased; a thin air-tight film of some petroleum compound having formed over the surface of the stoppers; and since 1880, or thereabouts, it has been necessary to take out the latter now and then, for a moment, when the bottles have not been in use for a long time, otherwise their extrication is exceedingly difficult, on account of a certain amount of vacuum produced between the surface of the petroleum and the stopper. This result is due to an absorption of oxygen by the sodium. It is evident, from many observations I have made, that this metal will draw oxygen from the air in the upper part of the bottle in spite of the naphtha, and in the course of a few months the partial vacuum thus produced can be appreciated by the marked resistance of the stopper to leave the neck of the bottle, though it can easily be turned round. It may be that sodium would deoxidise a resinified petroleum, and the deoxidised resinous matter, in its turn, absorb oxygen from the air of the bottle. Anyhow, a partial vacuum is produced, which, in the case of a large, thin, or defective glass bottle, might give rise to an explosion by external atmospheric pressure. But in the Swansea explosion it appears more probable that water or acid has had access to the metal after or during the evaporation of the naphtha, since some of the fragments of the metal strewn about were ignited; and the origin of this water or acid will have to be sought for. Petroleum is lighter than water and floats readily on the surface, but the oil can be mixed with a small quantity of water, and like many vegetable oils may be damp. The presence of even a small amount of water or acid would be sufficient to account for the accident; and the question arises—whether water or some organic acid may not be formed from impure resinified petroleum by the prolonged deoxidising action of sodium? and, whether any sulphuric acid used in purifying the naphtha may, in this case, have remained in it? The latter seems to me the most probable.

Not being acquainted with all the facts which surrounded the bottle of sodium at Swansea, and the possible impurities of its contents, I cannot, of course, enter into any more minute explanation of the extraordinary result recorded in the letter referred to above. We require more details.

Laboratory of Analytical Chemistry,
Putney, London, S.W.

THE DETERMINATION OF COBALT IN MANGANESE ORES, AND A QUICK METHOD FOR ITS ESTIMATION.

By THOMAS MOORE.

THE assay of the ores in question is one which, if not exactly presenting any great difficulty, is, nevertheless, exceedingly tedious, usually inconveniently long, and requires almost undivided attention throughout its entire course. At first sight there would appear to be no trouble in separating the iron and alumina from the cobalt, nickel, and manganese by treatment with ammonia hydrate or by sodic acetate, but a very short experience will suffice to demonstrate that the former is absolutely worthless, and that the basic acetates of the latter must be precipitated at least four times before one can be assured that the separation, as far as the cobalt is concerned, is sufficiently complete. The filtration, too, of these slimy precipitates requires the utmost patience, and the large bulk which

the filtrate too often assumes all tend to the consumption of much time.

The two methods which I give have been devised to avoid, or at least diminish, these inconveniences. The first process, although bearing no comparison to the second for rapidity, can be confidently relied upon to furnish rigorously exact results for a minimum expenditure of time, gives also easily filtered precipitates and filtrates of reasonable volumes. The second method, which I believe is quite new, gives results quite accurate enough for all technical purposes, and by paying careful attention to all sources of error will furnish figures which, for all practical purposes, are exact; but its great recommendation is that an hour is ample time for the complete operation.

First Method.—Two grms. of the ore are fused in a platinum basin for fifteen or twenty minutes with 4 or 5 grms. potassic bisulphate at the highest temperature a Bunsen burner is capable of giving. At the end of this time the mixture will be in a quiet state of fusion; remove the cover and (still continuing the heating) add a piece of ammoniac carbonate about the size of a pea, replace the lid, so as to avoid loss by spirting, and repeat the addition of the carbonate until the mass evolves the fumes of SO_3 but feebly, then pour the melt upon a clean slab of metal and allow to cool. About 400 c.c. of water are now raised to the boiling-point in a beaker of glass and the rose-coloured melt, together with the rinsings from the crucible, carefully added. The solution is then boiled for twenty minutes so as to ensure complete solution of all soluble matter. The insoluble residue is now allowed to settle, the clear liquid passed through a filter, and the insoluble matter, after being repeatedly boiled up with successive portions of water, is thrown on a filter and well washed with boiling water. The precipitate of silica and basic sulphates will be found on testing to be quite free from either cobalt or nickel and filters with the greatest facility. The filtrate is now heated, 30 c.c. acetic acid added, and a rapid stream of sulphuretted hydrogen passed through it; as soon as the small quantity of iron still remaining in the solution appears to be reduced, add about 50 c.c. of a strong solution of ammoniac acetate, when, if the solution has been kept boiling, all the cobalt and nickel will be precipitated. The sulphides so precipitated settle readily to the bottom of the flask, are very dense and compact, and much less liable to oxidation than when thrown down in the usual manner from cold solutions. After having been well washed, the precipitate is dried and then calcined at as low a temperature as is compatible with the thorough destruction of the filter paper, then dissolved in a few c.c. hydrochloric acid and converted into sulphates by evaporation with sulphuric acid. From the solution of the sulphate so obtained the two metals are electrolytically deposited in the usual manner after the addition of an excess of ammoniac hydrate; the small amount of peroxide of iron usually present floats in the solution and has no appreciable influence on the results. Having determined the joint weight of the two metals, they are then dissolved off the cone and their further evaporation carried out by any of the well known processes, the precipitation of the cobalt as the ammoniac phosphate being the most suitable.

Second Method.—This method admits of cobalt being directly determined in the presence of a large number of bodies, some of which present considerable difficulties by the usual modes of separation. The principle upon which it depends is that of the absorption of oxygen by ammoniacal solutions of cobalt; this absorption, when cobalt alone is present, is very energetic and complete, likewise in the presence of nickel or other salts which form soluble compounds with ammonia. Manganese, like cobalt, forms a double salt with ammonia, and this, too, on exposure to air absorbs oxygen. If, however, we take a solution of the two metals containing an excess of citric acid, then on adding ammonia it will be found that though the cobalt absorbs oxygen somewhat less energetically than before, the manganese has this property so much enfeebled that the

amount absorbed during the experiment is so small as to be negligible; the addition of citric acid having the effect of causing an ammoniacal solution of manganese to become practically indifferent to air. Taking, then, this fact into consideration, and remembering that citric acid effectually prevents the precipitation of iron or aluminium solutions by ammonia, it is easy to see how this can be applied for the cobalt assay by simply measuring the volume of oxygen absorbed; thus, leaving the ammonia out of the question, the formula is—



That this Co_2O_3 may be united to various proportions of NH_3 , forming different cobaltamines, does not affect the case, their formation being a matter of no moment so long as the total oxygen absorbed remains constant. There is therefore required for the oxidation of 118 grms. of cobalt 11,200 c.c. of oxygen at 0°C . and 760 m.m. pressure. Hence, for every c.c. (at the standard temperature and pressure) of oxygen absorbed there is 0.0105 of Co required.



Two grms. of the ore are taken for the assay and evaporated to dryness with hydrochloric acid; to the residue 3 grms. of citric acid dissolved in 3 or 4 c.c. of ammonia are added, care being taken that the acid is in slight excess; if alkaline, a drop or two of HCl must be added so as to obtain a *distinct* acid reaction. The residue and citric acid solution are now heated until all soluble matter is dissolved; 2 or 3 c.c. water may be added if too concentrated, and then allowed to cool. The solution is then transferred to the apparatus figured in the sketch, and the volume made up to the zero mark with water. A sufficiency of the strongest liquor ammonia saturated with ammoniac chloride is now injected in the usual manner with the Bunte gas burette, of which it will be noticed this is simply a modification, or a given volume of air may be withdrawn by placing a second burette filled with water alongside, and connecting the two by a piece of rubber tubing provided with a clip and filled with water, care being taken to exclude air bubbles, and allowing a portion of the water in the second to flow away; the requisite amount of ammonia (4 or 5 c.c.) can now be passed into the first burette by opening the lower tap. It is unnecessary to occupy space by going into further details, as the manipulation is in every respect similar to that of the well

known aforesaid burette. The apparatus is now well and violently shaken until all absorption ceases, which can be known by placing the lower orifice in a little ammonia and noting if the latter continues to enter the bulb on opening the tap. The ammoniacal liquid is now thoroughly displaced by a current of pure water, entering by the upper and passing away by the lower outlet, and if the duplicate burette has been employed the air abstracted must be transferred to the original by connecting as before and passing a current of water through both apparatus, entering by the lower tap of the second and passing away by the lower tap of the first. Having allowed the apparatus to attain a uniform temperature, the pressure of the enclosed gas is now corrected and brought, by any of the usual methods, to that of the atmosphere. There now only remains to be done the reduction of the volume of oxygen absorbed to the standard temperature and pressure, taking into account the tension of the water vapour, either by the formula—

$$V_0 = \frac{V 273 (B-f)}{(273 + t) 760}$$

or by the very convenient piece of apparatus first proposed by Williamson and Russel, and fully described in "Winckler's Quantitative Gas Analysis," page 35, German edition.

Too much attention cannot be paid to the taps; they must be perfectly air tight and frequently paraffined, as the leakages caused by them when badly fitted give rise to errors extremely difficult to detect. The apparatus should be placed in a tank of water for at least five minutes before taking measurements, so as to ensure a uniform temperature, and the solution must be thoroughly washed out of the burette first with pure water and then with a weak solution of some acid, to absorb any ammoniacal gas.

It should, perhaps, be mentioned that although the silica present in the ore is, of course, without influence upon the results, still it is better to filter it off, as the fine particles getting entangled in the glass tap soon render it useless. As already mentioned, the method leaves scarcely anything to be desired in the presence of nickel or other compounds forming soluble salts with ammonia, the oxidation being prompt and complete. With the employment of citric acid, the only difference is that the absorption is more gradual, and as the greater part of the cobalt becomes oxidised, the absorption becomes still slower; never, however, as far as my experience has gone, to such an extent as to exceed the time mentioned. Iron, it is hardly necessary to state, must, if present, be first converted into the ferric state.

New Caledonia, December 12, 1891.

CONTRIBUTIONS TO CELLULOSE CHEMISTRY.

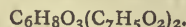
By C. F. CROSS and E. J. BEVAN.

THIS subject continues to attract investigators, and the past year has been distinguished by important communications, notably those of Tollens and his fellow workers, E. Schulze and W. Will (*Berl. Ber.*, 1891, 400, 694, 2277, 3575). In view of the rapid convergence of the lines of research followed by the workers in this field, we take the opportunity of recording a few brief notes of results obtained by ourselves, in anticipation of their fuller treatment, which we reserve until they may be regarded as completing a chapter in the development of the subject.

Cellulose Benzoates.—The hydrates of cellulose (cotton) obtained by precipitation from its solution in the ammonio-cupric reagent or in $ZnCl_2.HCl$ (*CHEMICAL NEWS*, lxiii., p. 66), are completely dissolved by solutions of the alkaline hydrates.

These solutions shaken with benzoyl chlorides, according to Baumann's method, yield a white curdy precipitate of a benzoate. After purification by solution in glacial

acetic acid, &c., it yields on analysis numbers corresponding with the formula of a *dibenzoate*—



This benzoate is soluble in acetic anhydride, and on boiling the solution with the addition of fused sodium acetate, a product is obtained which appears to be the triacetyl monobenzoate.

When cellulose is treated with a strong solution of sodium hydrate (15 per cent Na_2O), and the mixture of "mercerised" fibre and alkali shaken with benzoyl chloride, combination takes place, there is an increase of weight of 60–70 per cent, and the purified product yields on analysis numbers corresponding with the formula of a *monobenzoate*.

It appears, therefore,—retaining for the moment the C_6^* formula for cellulose—that of the five O-atoms four are capable of reacting as OH; that in the solution of the hydrate of cellulose in alkaline hydrate, two of the OH groups react with the alkali, which two are benzoated by reaction with the anhydrochloride, and that in the "mercerising" action of the alkaline hydrates one OH group only is brought into play. We now have, in the benzoates, acetates, acetobenzoate, and nitrates of cellulose, a fair range of ethereal derivatives which we have every reason to regard as simply related to the parent molecule. We have next to determine such physical constants for these derivatives as shall afford criteria of molecular weight and volume, and in this way to arrive at an approximate estimate of the reacting unit, or the molecule of cellulose.

Cellulose Terminology.—The researches of Schulze and others (*Berl. Ber.*, *loc. cit.*), chiefly upon the constituents of seed-tissues, have brought to light a variety of forms of cellulose, various in regard to the simpler carbohydrates into which they are resolved by hydrolysis, and of which, therefore, they may be regarded as the anhydro-aggregates. In addition to those which yield dextrose, there have now been brought to our knowledge cellulosic forms of mannose, galactose, arabinose, &c.

Some years ago we ourselves called attention to the fact that the celluloses of the *Graminæ* are differentiated by a characteristic colour reaction (rose-red) on boiling with solution of aniline sulphate, and by yielding furfural on hydrolysis. Schulze has isolated a number of celluloses yielding this aldehyd on hydrolysis, of which he has also determined the yield (*Berl. Ber.*, 1890, 2284).

The formation of furfural we now refer, on the basis of the researches of Tollens, to a pentagulosic molecule, a constituent of the celluloses in question. We ourselves usually observe that this aldehyd is accompanied by acetic acid in the distillate,†—an observation which, we think, should be followed up with a view to a possible further light on the mechanism of the hydrolysis. It is noteworthy that both furfural and acetic acid have the ratio $C_mH_{2n}O_n$, and their formation from any carbohydrate therefore involves empirically only a + or – of H_2O molecules.

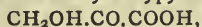
It is, perhaps, premature to adopt as final any of the proposed additions to the terminology of this wide group of plant constituents. We can only retain the original term cellulose as the substantive or group designation, and leave the adjectives to the struggle for survival.

Hydrolysis of Cellulose.—The remarkable results which have been obtained of late years from the study of the hydrolytic dissection of the starch molecule clearly indicate that for anything like a complete study of the molecular structure of the celluloses they must be subjected to a similar process of disintegration into known products. The study of the ethereal derivatives which we have been prosecuting is the exact converse of this; but while, however, it is not to be accorded precedence over first

* We propose, for reasons given (*infra*), to abandon the nC_6 for the nC_5 formula for (cotton) cellulose.

† From pure straw (oat) cellulose, by solution in H_2SO_4 in the cold, diluting and distilling, we have obtained 4–10 per cent of its weight of $C_5H_4O_2$, together with 3–5 per cent furfural.

principles, we are of opinion that valuable results are to be obtained by studying cellulose as a molecular aggregate. In the meantime, Messrs. Brown and Morris are making progress in the study of the "cytohydrolytic" ferment of the barley corn, and to them and others who are in the position of attacking the cellulose problem from the bio-chemical point of view we must look for light in this direction. The hydrolytic processes of the laboratory can hardly be expected to do more than reveal the nature of the ultimate constituent groups, *i.e.*, the simpler carbohydrates of which the celluloses are built up; and the more drastic decompositions, such as that brought to light by W. Will, who obtains hydroxypyruvic acid—



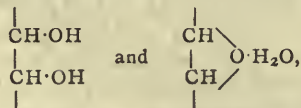
as a product of the resolution of cellulose nitrates by dilute alkaline solutions, are of course still less likely to show how the constituent groups are put together, although they cannot fail, of course, to throw valuable light upon their constitution.

Failing, therefore, in the meantime, any "natural" hydrolytic agent available for isolation and control to suit the exigencies of the laboratory, we can only continue in the two directions of study (a) of synthetical derivatives of simple relationship to the original molecule, and (b) of products of what we may term wholesale hydrolysis.

Constitution of the Celluloses.—It is obvious that for the present we must be content with general conclusions as to the constituent groups of the celluloses, and a suspension of judgment as to how they are put together. For the typical cotton cellulose the balance of evidence would lead us to adopt a C_{12} formula for the unit group, of which we may assume it to be the anhydro-aggregate.

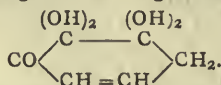
The main points in the evidence are the relationships of this cellulose to starch and the conclusions drawn from the study of the nitrates.* Of the ten oxygen atoms in such a formula, eight appear to be capable of reacting as OH oxygen. The two remaining there is every ground for regarding as in the form of carbonyl oxygen. In support of this we may cite (1) the formation of hydroxypyruvic acid as a product of resolution of the nitrates by dilute alkaline solutions in the cold (W. Will). (2) Our own observations, hitherto unpublished, of the formation of large quantities of acetic acid (10—20 per cent), by fusion of cellulose with alkaline hydrates at 300—400°; (3) the aldehydic and ketonic character of the products of resolution by simple hydrolytic processes.

The differentiation of the OH groups would be accounted for by proximity to a CO or a CH_2 group in the molecule; and the fact that the OH groups, at least in cotton cellulose, are latent rather than active, would be explained by assuming that in cellulose we have steps intermediate between—



such as we are familiar with in the hydrates of the inorganic oxides, water of crystallisation, &c.

Lignocelluloses.—The characteristic reactions of the lignocelluloses, typified by the jute fibre, we have referred to the presence of groups of the general form—



We have additional evidence in support of this view in a recent observation, that when jute is dissolved in the ZnCl_2 .HCl reagent and the solution treated with bromine, there is direct combination in the cold with the halogen. The quantity entering into combination being, moreover,

* We obtain from "soluble" starch treated by Baumann's method a benzoate similar to that from cellulose, and giving analytical numbers corresponding with a tetrabenzoate (C_{12}) formula.

one-half (the equivalent of) the chlorine combining with the fibre substance to form the characteristic quinone chloride (*Chem. Soc. Journ.*, vol. lv., 200).

In addition to these groups which appear to be condensed into complexes of C_{18} , *i.e.*, three C_6 groups, we have what we may term the cellulosic basis of the fibre, a cellulose which, when isolated, is found to resemble very closely the normal cotton and linen celluloses, the proportion of this being from 75—80 per cent of the raw fibre. This cellulose we may term cellulose α . The third constituent we had identified, at the time of publishing our last paper (*Chem. Soc. Journ.*, 1889, 200), as a carbohydrate yielding furfural and acetic acid as products of hydrolysis. By the action of chromic acid in presence of dilute acids in the cold we have succeeded in oxidising away the quinone constituent, leaving the carbohydrate in question in the form of a cellulose associated with the before mentioned cellulose α . We find that the yield of acetic acid (and furfural) is unaffected by the treatment, and the identification of this third constituent, or cellulose β , is therefore complete. The jute fibre, therefore, may be regarded as an anhydro-aggregate of:—

Cellulose α —Probably a dextroso-cellulose allied to cotton and linen cellulose.

Cellulose β —A penta-cellulose yielding furfural and acetic acid on hydrolysis.

Lignone—A C_{18} quinone or quinol converted by chlorination and reduction into derivations of the trihydric phenols.

We submit the above brief notes of results of current work, pending their completion and confirmation for an exhaustive communication to be submitted in due course to the Chemical Society, from whose Research Fund we have been fortunate in again receiving a substantial award.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

(Continued from p. 69).

THIS method may be expanded, as proposed by Mr. McElroy, so as to permit the estimation of other bases in the same portion of the material. For this purpose the filtrate and washings from the first precipitation are collected. Sufficient ammonium oxalate is added to them to precipitate the calcium. As the ammoniacal solution must be kept cool, this precipitate is very fine, and I have found that the only way to collect it satisfactorily is by using a Gooch crucible without pressure. By proper packing of the asbestos film, the filtration can be made quite rapid and satisfactory. The filtrate and washings are again collected, and a solution of sodium phosphate added to precipitate the magnesia. It is absolutely necessary to keep all solutions cold and ammoniacal during these operations, so as to prevent the separation of molybdic anhydride.

Of the methods lately proposed for the determination of iron and aluminium in phosphates the most prominent is the method of Glaser, also called the "alcohol method" (*CHEMICAL NEWS*, lxiii., p. 146).

Glaser proceeds as follows:—

5 grms. of the phosphate are dissolved in the usual manner in 25 c.c. nitric acid (specific gravity 1.20) and 12.5 c.c. of hydrochloric acid (specific gravity 1.20) and made up to 500 c.c. 100 c.c. of the filtrate are placed in a 250 c.c. flask with the addition of 25 c.c. of sulphuric acid (specific gravity 1.84). The flask is allowed to stand for five minutes, shaking occasionally. About 100 c.c.

* Read before the Washington Chemical Society, Nov. 12, 1891. From the *Journal of Analytical and Applied Chemistry*, Vol. v., No. 12.

of 95 per cent alcohol are added, the flask is cooled, made up to the mark with alcohol, and well shaken. After standing half an hour the liquid is filtered. 100 c.c. of the filtrate (=0.4 grm.) are evaporated down in a platinum capsule until the alcohol is expelled. The residual solution is mixed with 50 c.c. water in a beaker and brought to a boil. Ammonia is then added to the solution until the reaction is alkaline, but not whilst boiling, to avoid violent effervescence. The excess of ammonia is removed by boiling, the solution is allowed to cool, filtered, the precipitate washed with hot water, ignited, and weighed as ferric and aluminic phosphates.

Jones (*Zeit. fur Angew. Chemie*, 1891, No. 1, p. 3) investigated Glaser's method and found that—

(a) The amount of alcohol prescribed was not sufficient to precipitate all the calcium sulphate.

(b) The amount of sulphuric acid is much more than is actually necessary.

He therefore modified the method as follows:—

10 grms. of the substance are dissolved in nitro-hydrochloric acid, and the solution made up to 500 c.c. 50 c.c. of this solution (= 1.0 grm.) are evaporated down to 25 c.c., and, whilst hot, 10 c.c. of dilute sulphuric acid (1:5) added, the whole stirred and cooled. 150 c.c. of 95 per cent alcohol are then added, and after stirring, the solution is allowed to stand three hours. The calcium sulphate is then collected on a filter, washed with alcohol, and the filtrate and washings collected in an Erlenmeyer flask. The washing is complete when the last ten drops, after dilution with an equal volume of water, are not coloured red with a drop of methyl-orange.

The calcium sulphate, whilst moist, is transferred to a platinum crucible, the filter placed on it, the alcohol burnt off, and the filter incinerated. The calcium sulphate is then ignited and weighed. The contents of the flask are heated to expel the alcohol, the residue washed into a beaker, made slightly alkaline with ammonia, and again heated until all the ammonia is driven off. This is absolutely necessary, as otherwise the precipitate will be contaminated with magnesia. The precipitate is collected on a filter, washed four times with hot water or water containing ammonium nitrate, dried, ignited, and weighed.

An excess of ammonia is added to the filtrate and washings, the whole allowed to stand twelve hours, when the magnesia will have separated as ammonium-magnesium phosphate, which can be collected, ignited, and weighed as usual.

Immediately after the above methods were published, considerable discussion arose with regard to the presence of magnesia in the precipitate of iron and aluminium phosphates.

Theodor Meyer (*Zeit. fur Angew. Chemie*, 1891, viii., p. 243) states that unless all of the ammonia is driven off the precipitate will contain magnesia, and, on the other hand, continued boiling not only drives off the free ammonia, but also some of the combined, forming acid ammonium sulphate, which re-dissolves some of the precipitate. This, however, separates out again on standing.

K. Wohlrab (*ibidem*, 1891, p. 170) and von Gruber (*Zeit. fur Anal. Chem.*, xxx., pp. 206, 207), however, dispute Meyer's statement, reporting analyses of known mixtures.

It does seem improbable that during the short time which is required for the precipitation any appreciable quantities of magnesia could separate.

(To be continued.)

Action of Chlorine upon Certain Acetones of the Fatty Series.—Demetrius Vladesco.—This memoir, too lengthy for insertion, is the last portion of an investigation which has been interrupted by the death of the author.—*Bull. de la Soc. Chim. de Paris* vi., No. 11.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

January 21st, 1892.

Professor W. A. TILDEN, F.R.S., Vice-President, in the Chair.

MESSRS. L. W. Fulcher, Harry G. Myers, Ph.D., and Thomas Stephenson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Fielding Bond, M.D., Rastrick, Yorks; William John Atkinson Butterfield, 10, Tressillian Crescent, St. John's, S.E.; Robert Brooke Floris, 18, Ridgway Place, Wimbledon, S.W.; Alfred Thomas Gailleton, Tulloch House, Perth, N.B.; William Percy Hatton, 73, St. Quintin Avenue, North Kensington; Lionel Manfred Jones, Beaumont House, Llanelly; William Cossar Mackenzie, Tewfikieh College of Agriculture, Ghizeh, Cairo; Charles Stephen Meacham, 62, Earl Street, Maidstone; Thomas Skurray, Abingdon, Berkshire; James Sykes, 76, Lockwood Road, Huddersfield.

Of the following papers those marked * were read:—

*93. "The Estimation of Oxygen Dissolved in Water."

By MATTHEW A. ADAMS.

The author describes an apparatus in which the estimation of oxygen in water by Schützenberger's method may be carried out so as entirely to avoid the loss of oxygen by diffusion or its entry. The essential feature is a cylindrical laboratory vessel about 350 c.c. in capacity, 20 c.m. long, and 5 c.m. in diameter, provided with four small lateral tubulures midway from the closed ends. By means of these it is attached to two burettes, one containing the indigo carmine, the other hyposulphite solution, and also to a mercury reservoir and to a Y-tube, one branch of which is connected with a supply of the water to be examined, the other serving as an outlet for the water. The tubes are all controlled by pinchcocks. The water and the liquids for titration are sucked into the vessel by lowering the mercury reservoir, and are subsequently discharged by raising it again; the tubes passing into the vessel from the burettes are provided with india-rubber valves which prevent either reflux or diffusion taking place into the burettes.

The author then refers to the peculiar irregular manner in which the action is known to take place, and describes his own observations, giving the results both of experiments made in the manner directed by Schützenberger and in the indirect manner recommended by Roscoe and Lunt (*cf. C. S. Trans.*, 1889, 552). From the results he concludes that in estimating oxygen by the Schützenberger process, the result obtained is liable to differ according to the rate at which the determination is effected, it being always higher when the titration is quickly performed.

*94. "The Luminosity of Coal-gas Flames." By VIVIAN B. LEWES.

The author has quantitatively studied the actions which lead to loss of luminosity in a Bunsen flame.

The volumes of varying mixtures of nitrogen and oxygen required to render 16.3 candle coal-gas non-luminous in a Bunsen burner are shown in the following table:—

Gas.	Volume of mixture required.	Composition of mixture.		Volume of oxygen present in amount required.
		Nitrogen.	Oxygen.	
I vol. ..	2'30	1	nil	nil
I " ..	2'30	5	I	0'38
I " ..	2'27	4	I	0'45
I " ..	2'02	3	I	0'50
I " ..	1'49	2	I	0'50
I " ..	1'00	I	I	0'50
I " ..	0'50	nil	I	0'50

It is evident that until the percentage of oxygen reaches the amount present in the atmosphere, the diluting influence of the nitrogen is so strong that it prevents the oxygen having any practical effect in destroying luminosity; but that as soon as the quantity of oxygen present has risen above 25 per cent, then its activity has so far overcome the diluting influence of the nitrogen that the latter has ceased to exercise any retarding influence on it.

In the case of other gases the results are as follows:—

1 vol. of coal-gas requires 0.5 vol. of oxygen.			
" "	1.26	"	carbon dioxide.
" "	2.30	"	nitrogen.
" "	2.27	"	air.
" "	5.11	"	carbon monoxide.
" "	12.4	"	hydrogen.

It is shown by experiment that dilution has the effect of destroying luminosity by greatly increasing the temperature necessary to decompose heavy hydrocarbons with liberation of carbon, so that at the temperature existing in a flame a volume of gas which undiluted will deposit 0.22 gm. of carbon, when diluted with 2.3 vols. of nitrogen will only deposit 0.0013, but the higher the temperature the less is the retarding action.

Experiments are next described in which the effect of the surrounding air on a flame is examined, and it is shown that, although the air introduced into a Bunsen is capable of bringing about certain changes in the flame when already burning in air, yet that it is quite unable by itself to keep the flame burning.

When a Bunsen burns under normal conditions, it has a bluish central zone, but if the air supply be largely in excess of that required for non-luminous combustion, the flame becomes smaller and fiercer with formation of a green central zone, which marks the change from a combustion in which the diluting influence of the nitrogen is still playing a certain part in causing non-luminosity, to a combustion in which the oxygen present having exceeded 0.5 vol. for each volume of gas, the nitrogen has ceased to exert any retarding influence.

By means of a platinum, platinum-rhodium thermocouple, the temperature was determined in various parts of a non-luminous Bunsen flame, burning 6 cubic feet of coal-gas per hour.

Point in flame.	Flame rendered non-luminous by—			Luminous flame. from Bunsen.
	Air.	Nitrogen.	Carbon dioxide.	
$\frac{1}{2}$ inch above burner	54°	30°	35°	135°
$1\frac{1}{2}$ " "	175	111	70	421
Tip of inner cone ..	1090	444	393	913
Centre of outer cone	1533	999	770	1328
Tip of outer cone ..	1175	1151	951	728
Side of outer cone level with tip of inner cone . . .	1333	1236	970	1236

A determination was made of the temperatures existing during the normal and also the "green centre" combustion of a Bunsen:—

	Blue inner cone.	Greenish inner cone.
Tip of inner cone	1090° C.	1575° C.
Centre of outer cone ..	1533 "	1600 "
Tip of outer cone	1175 "	1545 "
Side of outer cone level with the tip of inner cone	1333 "	1511 "

Analyses of gases extracted from luminous flames at the points at which the temperatures had been determined show that in the inner zone there is a rapid diminution in the quantity of hydrogen as the gases ascend in the centre of the flame, a slow diminution in the quantity of the unsaturated and saturated hydrocarbons, and a large increase in the quantity of carbon monoxide in the first half of the flame. Analysis also revealed the fact that the

outer non-luminous zone of a flame is not an area of complete combustion, but a portion of the flame in which the rapid entrance of air cools, dilutes, and finally puts out the flame, allowing not inconsiderable amounts of methane, carbon monoxide, acetylene, and even hydrogen, to escape unburnt.

The undoubted presence of acetylene in the products escaping from the flame, and the fact that the incomplete combustion of hydrocarbon gases always gives rise to the formation of this compound, suggested the idea that it might play an important part in the changes taking place in the interior of a flame, and experiments were made to ascertain if any appreciable quantity were formed during the destruction of the hydrocarbons in the flame gases.

	Total unsaturated hydrocarbons. Per cent.	Containing acetylene. Per cent.
Gas in burner	4.38	0.035
$\frac{1}{2}$ an inch above rim of burner .	4.00	0.340
$1\frac{1}{2}$ inches " "	1.53	0.560
Tip of inner cone	1.98	1.410
Centre of luminous zone .. .	0.45	0.045
Tip of luminous zone	nil	nil

It would therefore seem that in the interior of the luminous flame the hydrocarbons are at once attacked by the small proportion of air which penetrates into the inner zone and that their incomplete combustion gives rise to acetylene, which by the time the top of the inner non-luminous cone is reached, constitutes over 70 per cent of the unsaturated hydrocarbons present, some of the acetylene, however, having probably been formed by the interaction of methane and carbon monoxide. A small proportion of some more stable unsaturated hydrocarbon may remain undecomposed and penetrate into the luminous zone, but the chief effect is due to the acetylene which is decomposed by the higher temperature, and the liberated carbon being for a moment heated to incandescence gives luminosity to the flame.

In the case of a flat luminous flame from a No. 7 Bary burner, the following results were obtained:—

Portion of flame.	Total unsaturated hydrocarbons. Per cent.	Containing acetylene. Per cent.	Other unsaturated hydrocarbons. Per cent.
$\frac{1}{2}$ an inch from burner	3.565	0.115	3.450
$1\frac{1}{2}$ inches " "	2.063	1.303	0.760
$1\frac{1}{2}$ " " "	1.393	1.133	0.260
$2\frac{1}{2}$ " " "	trace	trace	nil

The author, therefore, regards the formation and decomposition of acetylene as the main cause of luminosity in a hydrocarbon flame, and if it be necessary for purposes of simple description to divide the luminous flame into zones, he thinks it would be most accurately regarded as consisting of three, viz:—

- I. The inner zone, in which the temperature rises from a comparatively low point at the mouth of the burner to about 1000° C. at the apex of the zone; in this portion of the flame various decompositions and interactions occur, which culminate in the conversion of the heavier hydrocarbons into acetylene, carbon monoxide being also produced.
- II. The luminous zone, in which the temperature ranges from 1000° C. up to a little over 1300° C. Here the acetylene formed in the inner zone becomes decomposed by heat with liberation of carbon, which at the moment of formation is heated to incandescence by the combustion of the carbon monoxide and hydrogen, thus giving luminosity to the flame.
- III. The extreme outer zone. Here, combustion being practically completed, the cooling and diluting influence of the entering air renders a thin layer of the flame non-luminous, finally extinguishing it.

This description of a luminous flame is of necessity far from complete, as it leaves out of consideration the causes which lead to the formation of the acetylene and the numerous interactions which take place between the products of combustion and the carbon in the upper zone of the flame.

The various actions which tend to cause the loss of luminosity in a Bunsen burner, in the author's opinion, may be summarised as follows:—

- I. The chemical activity of the atmospheric oxygen, which causes loss of luminosity by burning up the hydrocarbons before they, in their diluted condition, can afford acetylene.
- II. The diluting action of the atmospheric nitrogen, which, by increasing the temperature necessary to bring about the partial decomposition of the hydrocarbons, prevents formation of acetylene, and in this way will, by itself, cause non-luminosity; in the normal Bunsen flame it acts by doing this until destruction of the hydrocarbons by oxidation has taken place.
- III. The cooling influence of the air introduced, which is able to add to the general result, although the cooling is less than the increase in temperature brought about by the oxidation due to the oxygen in the air.
- IV. In a normal Bunsen flame the nitrogen and the oxygen are of about equal importance in bringing about non-luminosity, but if the quantity of air be increased, then oxidation becomes the principal factor and the nitrogen practically ceases to exert any influence.

DISCUSSION.

Professor SMITHELLS said he thought Professor Lewes had made an important contribution to the subject of flame, though, perhaps, some of his conclusions were rash and open to criticism. He directed Professor Lewes' attention to the controversy on the cause of delumination of flames which had taken place between Blochmann and Heumann (*Annalen*, ccvii., 167; *Ber.*, xiv., 1250, 1925, 2210), in which the whole question was very fully discussed and dealt with in a quantitative manner; also to Waldie's observations (*Phil. Mag.* (1838), No. 13, p. 88), in which delumination was effected by introducing luminous flames into atmospheres containing gases neutral to combustion. Waldie also made quantitative measurements, and sought to establish a relationship between diffusibility and deluminating effect. The abnormally great effect of carbon dioxide in destroying luminosity had been generally attributed, not to its high specific heat, but to its power of taking up carbon. Thus, for example, when mixed with an equal volume of ethylene in a flame, it was supposed that it underwent conversion into an equal volume of methane and a double volume of carbon monoxide—both of which would burn with practically non-luminous flames. Professor Lewes was in error in stating that Davy limited his theory to flames produced by hydrocarbons, for he explicitly stated that the luminosity of all flames ordinarily called luminous was to be attributed to solid particles, and in this respect left his theory open to Frankland's correction; he was also wrong in supposing that the theory that carbon is separated in a flame, owing to preferential combustion, was no longer held: it was, on the contrary (as the speaker could vouch from careful investigation), very widely accepted and taught. In a paper which is in the press it would be clearly demonstrated, he thought, that there are four distinct regions in a flame, however many gradations of chemical change there may be. He considered that the most important point in the paper which they had heard was that relating to the presence of acetylene in the flame. In his own experiments with ethylene he had also found that during luminous combustion scarcely any other hydrocarbons than acetylene are present in the aspirated gases. He was not satisfied, however, with Professor Lewes' proof of the escape of acetylene from

ordinary luminous flames; whilst there was no *a priori* evidence against such an occurrence, unless the extraction of acetylene had been effected otherwise than by introducing cold aspirating tubes into the flame, it might be that the production of acetylene was a consequence of the method of experiment—it being well known that acetylene escaped freely from flames in contact with metallic surfaces. Accepting it as proved that the formation of acetylene in flames was an important factor in the origin of luminosity, the question was by no means worked out. It remained to discover exactly what became of the acetylene. Professor Lewes had kindly left the solution of this problem to the speaker, who, however, on his part, expressed a desire not to lay claim to too much undiscovered country, or to preclude Professor Lewes from the natural continuation of his interesting investigation.

Professor LEWES, in reply, said that he was perfectly aware of the work done by Heumann, Blochmann, Stein, and Wibel. He must, however, dissent from the assumption that they had given quantitative proofs of many of their assertions.

The theory that carbon dioxide acted in destroying luminosity by converting ethylene into carbon monoxide and methane was, he thought, disproved, both by the experiments on the effect of heat in restoring luminosity to the flame and by the thermal changes taking place, as shown by the temperature of the diluted flame.

Undoubtedly Sir Humphry Davy went rather too far in his theory of luminous flames; but in a paper on the subject by him, in the *Phil. Mag.* for 1817, he says: "The intensity of light of flames depends principally upon the production and ignition of solid matter in combustion," also "Flame is gaseous matter heated so highly as to be luminous," and "when in flames pure gaseous matter is burnt, the light is extremely feeble," so that it seems hardly just to insist that he considered solid matter absolutely essential to luminosity.

The determination of the combustible gases escaping unburnt from the outer zone of non-luminous flames had been made by taking a platinum tube 2 m.m. in diameter, bent into a ring, and pierced on the inside with minute holes; this ring was placed round the flame, but not in contact with it, and the products of combustion were aspirated through this, so that the acetylene could not be due to the action of the tube.

The speaker regarded the conversion of the hydrocarbons into acetylene as the chief cause of luminosity in flame, because acetylene was practically the only heavy hydrocarbon present in that part of the flame where luminosity commenced, and as it was known that acetylene was an endothermic compound, which could be decomposed by detonation, it seemed highly probable that it would be readily decomposed by heat and liberate carbon.

With reference to Mr. Groves's remark that when a Bunsen burner is alight at the bottom, a non-luminous flame is produced, as the acetylene escapes unburnt, such a flame could only have a low light value.

*95. "The Origin of Flame Colouration. A Preliminary Notice." By A. SMITHELLS.

The author has found that the two cones of non-luminous flames separated widely from one another by the apparatus recently described by him in conjunction with Mr. Harry Ingle (*cf. Proc. Chem. Soc.*, 1891, p. 159), are differently affected by certain flame-colouring compounds. The most conspicuous case is that afforded by copper salts. In the inner cone of such a flame, copper salts produce no effect or only a lurid luminosity, without the slightest tinge of green, whilst in the outer flame the usual green colour is fully developed. Similar differences are noticed when using manganese salts. On introduction of gold chloride, the outer flame assumes a green and a blue tinge; the green, which is said to be the colour characteristic of gold salts, is not observable in the inner flame, but only a blue colour and general luminosity. The

salts of the alkalies and alkaline earths appear to affect both cones alike.

As the inner cone is very much hotter than the outer one, the non-development in the former of the usual colouration is not to be attributed to any deficiency in temperature. The only explanation which suggests itself is that in some cases at any rate the colouration of flames is not to be attributed to the mere volatilisation of salts and the incandescence of their dissociated or undissociated vapour, but to a *flash* accompanying chemical combination. The particular combination, which in the case of copper gives rise to a green flame, may be that of the metal with oxygen. In the experiment cited, the inner cone of flame is surrounded by an atmosphere of carbon monoxide and dioxide, hydrogen, and water, which is capable of reducing copper compounds, even at a red heat, whereas the outer cone is surrounded by oxygen. The view here advocated is confirmed by the effects noticed on introducing copper oxide dust into the gas-supply. As the dust passes through the inner cone, a mere general luminosity due to solid particles is noticed, but when it reaches the outer cone it colours this a bright green. The copper oxide appears therefore to be reduced to metal in the inner cone, and to be re-oxidised in the outer one, the act of oxidation giving rise to the green flash of light.

The hypothesis here broached, that flame colourations are due in some cases to chemical actions, and are not mere physical effects, requires for its support a greater array of facts and much more careful investigation than are here recorded. The author is engaged in extending the investigation, and only brings the matter forward at the present time after hearing that the flame-separating apparatus is likely soon to come into general laboratory use.

*96. "Note on the Action of Dilute Nitric Acid on Coal." By R. J. FRISWELL.

In the last number of the *Berichte* (1891, p. 4085), Lutz has described the action of nitric acid on graphite, certain varieties of which, on treatment with the strongest fuming acid, yield a product which "puffs" like a nitro-compound when heated on platinum foil, and then swells out into prolonged vermiform coke-like masses. The writer feels that the substance in question sufficiently resembles one he has quite lately discovered to cause him to communicate the following note:—

If bituminous coal in fine powder be covered with rather more than double its weight of 49 per cent nitric acid, the mass rapidly becomes warm, and dense red fumes are given off. If 90 grms. of coal and 200 c.c. of the acid are taken, the action is extremely brisk and the frothing so violent that a 2000 c.c. flask is requisite to contain the mass. In about thirty minutes the action slackens, and heat being now applied the action is kept going at such a rate that a brisk evolution of gas continues; the solution is gradually raised to the boiling-point and there maintained, the total time occupied being about six hours. The whole is now diluted, poured into a filter, and well washed. The filtrate consists of dilute nitric acid, with salts of calcium, iron, &c., in solution. The black residue on the filter is apparently unchanged coal. When washed free from acid, the residue is introduced into a flask and boiled with a dilute solution of sodium carbonate; nearly the whole dissolves, carbonic anhydride being briskly evolved. The resulting deep black-brown coloured liquid filters with great difficulty, but by careful treatment with water in deep vessels the insoluble matter from the 90 grms. of coal was found to be 12.5 grms., consisting of coarse particles of coal, sand, &c.

One grm. of coal, ground in an agate mortar and similarly treated, left only a trace of insoluble matter, so that, in some varieties of coal at least, the whole of the organic matter of the coal undergoes change.

The filtered solution on acidification with (preferably) hydrochloric acid, deposits a bulky, deep brown-black, flocculent precipitate, which is difficult to wash; it is in-

soluble as long as the wash-water contains small quantities of metallic salts or acids, but dissolves somewhat freely as the washing proceeds. In boiling distilled water it is fairly soluble, and separates therefrom on cooling in deep brown flocks.

The washed acid dried at 100° forms brilliant, black, friable masses, showing bright conchoidal fractures. If heated on platinum foil it puffs, swells slightly, and leaves a residue of carbon rather more bulky than its original mass, and almost as brilliantly black. The puffing is very like that of a nitro-compound with a very high carbon ratio; attempts to reduce it with zinc dust and caustic soda and with sodium amalgam have hitherto failed, and so have similar attempts with acid reducing mixtures. The presence of nitrogen is indicated in the usual manner on heating it with sodium; on submitting it to dry distillation with zinc dust, hydrogen and cyanogen are evolved, a small aqueous distillate, smelling of ammonia and faintly of pyridine, and containing a very large quantity of hydrocyanic acid, being also obtained.

If the black acid be further treated with nitric acid, a brown acid is formed, which has not yet been examined.

At first sight the product appears to bear considerable analogy to the humic and ulmic acids described in vol. xv. of "Gmelin's Handbook," particularly the one known as Sprengel's humic acid, obtained by extracting peat with ammonia. It, however, differs very much from that product in several particulars. It is not hygroscopic, it does not become insoluble on drying, and it does not yield acetic acid on dry distillation. As to the other humic acids, the substance from coal does not yield ammonia when boiled with alkalies, as they all, or nearly all, are said to do.

Lastly, there is very strong evidence in favour of the new product being a nitro-compound.

The possibility of attaining some evidence through the study of the substance in question as to the character of the constituent of coal from which it is derived is obvious.

97. "A Pure Fermentation of Mannitol and Dulcitol." By PERCY F. FRANKLAND, F.R.S., and WM. FREW.

The authors have obtained a micro-organism which sets up a fermentative decomposition not only of mannitol but also of dulcitol, which has not hitherto been subjected to pure fermentation, and which has been found to resist the fermenting bacteria with which they have hitherto experimented.

The products of the activity of this organism are essentially the same in the case of the two substances in question, consisting of ethyl alcohol, acetic acid, succinic acid, carbonic anhydride, and hydrogen, a notable proportion of formic acid being also obtained when the fermentation occurs in the absence of air and under slight pressure.

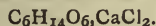
The carbonic anhydride and hydrogen evolved are approximately in the proportion of equal molecules or in that in which they are present in formic acid, and owing to the variable quantities in which the formic acid was discovered in the several fermentations, it is believed that more or less of the formic acid at first produced is subsequently decomposed with evolution of equal numbers of molecules of carbonic anhydride and hydrogen. This is the more probable, as in each of the fermentations the sum of the formic acid, hydrogen, and carbonic anhydride approximately corresponds in molecules of formic acid to the amount of alcohol in molecules produced in the same fermentation.

The decomposition of the dulcitol and mannitol may be regarded as involving two independent sets of changes, viz., (a) $C_6H_{14}O_6 = 2C_2H_5O + CO_2 + CH_3CO_2$ and (b) $C_6H_{14}O_6 = C_4H_6O_4 + C_2H_4O_2 + 2H_2$; but from the proportion which the acetic acid bears to the alcohol, it appears that two molecules are resolved in accordance with equation (a) for every one that is decomposed according to (b). The only marked discrepancy is in the case of the succinic acid, which was only found to about half

the extent demanded by the equations given, but this discrepancy is probably due to the difficulty attending the accurate determination of succinic acid in a complex mixture of substances such as was present in these experiments.

In view of the products to which this organism gives rise, the authors propose for it the name of *Bacillus ethacetosuccinicus*. A detailed account of its morphological characters by Mrs. Percy Frankland is appended to the paper.

The authors mention that incidentally a compound was discovered of dulcitol with calcium chloride,—



98. "Synthesis of Hexahydrotetraphthalic Acid." By J. E. MACKENZIE and W. H. PERKIN, Jun., F.R.S.

By eliminating two molecules of carbon dioxide from the hexamethylenetetra-carboxylic acid obtained in the form of ethylic salt by the interaction of ethylene bromide and the disodium derivative of ethylic butanetetra-carboxylate, the authors have obtained as chief product the sparingly soluble hexahydrotetraphthalic acid of von Baeyer, together with a small amount of what is probably the isomeric acid.

99. "The Magnetic Rotation of Dissolved Salts." By W. OSTWALD.

In a former paper (*C. S. Trans.*, 1891, p. 198) I pointed out that the unexpected results which Dr. Perkin obtained in his investigations on the rotatory power of solutions might be explained by means of Arrhenius's electrolytic dissociation theory, at the same time suggesting that the rotatory power of the ammonium salts of weak acids would probably show marked deviations from the calculated values.

Dr. Perkin, however, states in a recent communication (*ibid.*, 1891, p. 981) that such deviations do not exist, the actual differences being very small and comparable with those attending the formation of the ethereal salts of the same acids. Although I must confess that this result is contrary to my expectations, I am anxious to point out that the fault is mine, and not that of the dissociation theory. According to this theory, the condition of a substance is very different according as it can act as an electrolyte or not, e.g., sodium chloride in the solid state or in aqueous solution; hydrogen chloride dissolved in amyl oxide (where it is a non-electrolyte) or in water, &c. In the case of the magnetic rotations of haloid salts, the differences foreshadowed by the dissociation theory are apparent as very considerable differences from the calculated values, and inasmuch as the former views did not take any account of such differences, I was right in saying that the dissociation theory is alone in accordance with Dr. Perkin's observations. The values for oxy-acids also differ from the calculated values, though in a much less degree; I expected such differences to be manifest also in the case of ammonia and the fatty acids, but Dr. Perkin has shown that the differences are quite insignificant.

As the dissociation theory does not lead to any numerical value or sign of the differences, the very low values observed by Dr. Perkin in the case of the fatty acids are not contrary to the theory, but suggest only the interesting question: on what qualities does the sign and the value of the variation of magnetic rotation attending the transition of non-electrolytic molecules into ions depend? In the case of haloid acids and salts, the variation is positive; in the case of the oxy-acids, negative; therefore, it is not surprising that molecules with nearly zero variations are also capable of existence. Investigation of a greater number of such cases will certainly throw light on this question.

A tolerably short method of testing whether my attempt to explain the facts of magnetic rotation by the dissociation theory is tenable, is the following:—As the greatest differences are observed in the case of halogens between the ionic and the non-ionic state, an investigation of

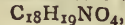
electrolytes containing halogen atoms, but not as ions, appears to promise most, e.g., the salts of mono-, di-, and trichloroacetic acids, of chloric and iodic acids, potassium mercuric iodide, K_2HgI_4 , &c. If in all these cases abnormal high values for the halogens should be obtained, I should not hesitate to confess that I have been on a false track.

100. "The Dissociation of Nitrogen Peroxide." By W. OSTWALD.

Availing himself of the data recently given by Cundall (*C. S. Trans.*, 1891, 1076), the author has compared the extent to which this compound undergoes dissociation when vaporised with that which it suffers when dissolved in chloroform; from the results he concludes that it behaves in accordance with Van't Hoff's generalisation that dissolved substances obey the same laws as gases. It appears, however, that in the gaseous state dissociation is far more advanced than in a chloroform solution.

101. "Corydaline." (I.) By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER.

Analyses of the alkaloid, as well as of its salts and derivatives, led Herm. Wicke (*Annalen*, 1866, cxxxvii., 274) to assign to corydaline the formula $\text{C}_{18}\text{H}_{19}\text{NO}_4$. The authors have purified samples by repeated re-crystallisation from a mixture of alcohol and ether, and have obtained the alkaloid in the form of flat, prismatic, colourless crystals, melting at 134.5° . In analysing it, they obtained results irreconcilable with Wicke's formula,—



and propose instead the formula $\text{C}_{22}\text{H}_{28}\text{NO}_4$.

The iodhydride is easily obtained in pale yellow coloured prisms by re-crystallising from water the precipitate obtained when a solution of potassium iodide is added to one of corydaline hydrochloride.

The platinichloride and corydaline methiodide were prepared by the methods described by Wicke.

The results obtained on analysing these compounds corroborate those afforded by the alkaloid.

When heated with hydrogen iodide, one formula-weight of corydaline yields four molecular proportions of methyl-iodide, together with the iodhydride of a base which apparently bears the same relation to corydaline that papaveroline bears to papaverine. On oxidation with potassium permanganate, corydaline yields a number of products which the authors are now engaged in investigating.

102. "Silver Compounds of Thiourea." By J. EMERSON REYNOLDS, F.R.S.

In a paper on some derivatives of thiourea, published by the author in 1888 (*Trans.*, liii., 857) it was pointed out that a crystalline compound of silver bromide with thiourea, viz., $(\text{CSN}_2\text{H}_4)_2\text{AgBr}$, was obtained by the interaction of equimolecular proportions of silver nitrate and the new compound then described, $(\text{CSN}_2\text{H}_5)_4\text{NBr}$. It was further stated that analogous compounds with other silver salts had been obtained by the same method as well as by direct union with thiourea, and that their detailed examination had cleared up certain obscure facts which were simply recorded in the author's earlier papers on thiourea.

The publication of a paper on the subject was deferred in the expectation of the completion of a new examination of the more interesting gold and platinum compounds, but the appearance of a paper by Kurnachow in a recent number of the *Berichte* on silver compounds of thiourea renders further delay undesirable, as that chemist refers only to the author's paper on thiourea, published 22 years ago.

In the course of the work of 1888, referred to above, the writer obtained the following compounds:—

$(\text{CSN}_2\text{H}_4)_3\text{AgNO}_3$. Beautiful long needles, melting at 141° , decomposing at 150° with separation of Ag_2S . Best obtained from an alcoholic solution containing 4 mols. thiourea to 1 mol. silver nitrate.

$(\text{CSN}_2\text{H}_4)_2\text{AgNO}_3$, a product of the partial decomposition of the previous compound by water.

(CSN_2H_4) AgNO_3 , a precipitate obtained on mixing equimolecular proportions of its constituents. This is decomposed by water; and the author regards the silver precipitate mentioned in his 1869 paper as the probably indefinite product of too carefully washed 1:1 compound above mentioned: this being the view also taken by Kurnachow.

(CSN_2H_4) $_2\text{AgBr}$, fine prisms melting at $120-121^\circ$.

(CSN_2H_4) AgBr , a white powder.

(CSN_2H_4) $_2\text{AgCl}$, crystalline; melts at $170-171^\circ$, decomposing at 180° . This was also obtained by Volhard.

No 1:1 compound was obtained with AgCl .

(CSN_2H_4) AgI , a white crystalline precipitate. In this case the higher compound appears only to exist in solution of thiourea.

(CSN_2H_4) $_2\text{AgCN}$. Small crystals which discolour at 115° and melt to a dark liquid at 126° sharply.

All the foregoing substances readily afford Ag_2S when heated a few degrees beyond their melting points, or even before melting, as in the case of the silver cyanide compound.

Anniversary Meeting and Second Anniversary Dinner.

The Anniversary Meeting will be held at *Four o'clock in the Afternoon* of Wednesday, March 30th next.

It is arranged that on the evening of the same day the Fellows and their friends will dine together at the White-hall Rooms, Hôtel Métropole.

NOTICES OF BOOKS.

The Phosphates of America: Where and How they Occur, How they are Mined, and What they Cost. With Practical Treatises on the Manufacture of Sulphuric Acid, Acid Phosphate, Phosphoric Acid, and Concentrated Superphosphates, and Selected Methods of Chemical Analysis. By FRANCIS WYATT, Ph.D. Second Edition. New York: The Scientific Publishing Co.

THIS is a very comprehensive work. After general remarks on phosphates and their assimilability, the author proceeds to his more special subject, the phosphates of North America. Here we must refer to a practical defect for which the publishers only can be held responsible. The running title at the head of each page is the same throughout, "The Phosphates of America." It would, we submit, have been a great convenience for the reader if these words had been placed at the top of the left hand page only, giving on the right hand the special subject of the chapter. This would be the more useful as there is no table of contents. Chapter III. is taken up with an account of the apatite deposits of Canada and their present exploitation. Chapter IV. describes the phosphate beds of South Carolina. We are told that "the known available and readily accessible deposits are all appropriated," and that the mines will, at the present rate of production, be all exhausted in about twenty-eight years from the present time. In Chapter V. follows a description of the deposits of Florida; whilst these deposits are of immense extent, and while they yield a material well suited for the manufacturer, a word of warning is thrown out which we cannot discuss, but which will be very salutary to intending investors.

Chapter VI. describes the manufacture of sulphuric acid, including the construction and use of the Glover tower. We regret to find that the writer persists in the use of the Beaumé hydrometer,—an instrument which has no advantages to compensate for its unquestionable defects.

In Chapter VII. we come to the manufacture of superphosphate, phosphoric acid, and high grade superphosphate. Dr. Wyatt pronounces the rejection of mineral phosphates

containing more than a certain limit of iron and alumina, i.e., 3 per cent, a "foolish prejudice." As a "dryer" he adds to the material "finely-powdered chalk or any other cheap and available source of carbonate." It is undeniable that an escape of CO_2 lightens the texture of the superphosphate. The custom of calcining Florida phosphate he considers "unscientific and harmful," since the presence of free lime retards the drying action. Some makers, however, after calcining, treat with an excess of water, thus dissolving away the lime and enriching the raw material.

The plant for the manufacture of superphosphate is described, and well figured. The author strongly recommends high grade superphosphates made with phosphoric instead of sulphuric acid, the economy of which he demonstrates at length. The only difficulty lies in getting the consumer to recognise its merit, and to pay a fair price for it.

The fumes given off from superphosphate works have not escaped public notice in the United States, and Dr. Wyatt accordingly gives a drawing of an absorption apparatus.

As regards the analysis of materials, the author gives processes for determining moisture, combined water and organic matter, silica, phosphoric anhydride, SO_3 , fluorine, lime, magnesia, carbonic anhydride, iron, and alumina. For the determination of carbonic anhydride he prefers the apparatus and method of Scheiller. The volumetric processes for determining phosphoric acid he has discarded for commercial purposes, though he retains the uranium method as a factory guide.

In his method of analysing pyrites we may mention as something exceptional that he determines the copper he precipitates as the white sub-sulphocyanide.

In the table of atomic weights, stated as being according to the latest determinations, platinum is still given as higher than gold. The work may be pronounced a very useful manual of reference.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—As your columns have always been open to any discussion which tends to the advancement of our profession may I ask for space to draw attention to a "circular" signed by Mr. William Thomson, of Manchester, and recently sent to Members of the Institute, inviting them to turn out the Council and elect one nominated by Mr. Thomson and his committee. My object in doing this is to point out two of the many inaccuracies in the letter.

No. 1.—The circular quotes, or rather misquotes, p. 7 of the Charter as follows:—

"The elevation of the profession of Analytical Chemistry and the promotion of the efficiency and usefulness of persons practising the same."

In the original it reads "profession of Consulting and Analytical Chemistry."

As the omission of this word—and indeed the whole tenor of the circular—would make it appear as if the Institute were founded for the advancement of Analysts rather than of the Chemical profession, ill-natured people might be inclined to think that this strange perversion of the wording of the Charter was not entirely undesigned on the part of the authors of the circular.

No. 2.—Under the heading "Fourth," the circular reads—"A distinct pledge was given that the papers and discussions of last year's conferences should be published."

This statement is—to speak quite plainly—untrue. The only document I can find relating to the matter is the notice issued by the Institute and dated December 11th,

1891, for the purpose of calling a meeting to consider the ethics of professional certificates. And this says—"The Council hope you will be able to attend" . . . "as a full report of the proceedings will not be published" (the italics are mine). This "*not*," like the word "Consulting" previously alluded to, seems to be ignored by the gentlemen who drew up the "circular."

The names of some fifty members of the Institute, nearly all public analysts, are appended to this circular, but I feel sure that neither Mr. W. Thomson nor these gentlemen would have consented to their names being attached to a document which they knew contained garbled quotations or untrue statements. There can be little doubt, therefore, that those who drafted the circular, and are responsible for the "inaccuracies" in it, considered "a policy of secrecy and silence" to be best when they were persuading their friends to allow their names to appear as approving of the circular.

It is to be hoped that the Members of the Institute at large will do their best to frustrate this attempt to hand over the Institute bound hand and foot to the public analysts, or rather to the small and noisy "party of progress" (?) who form but an exceedingly small fraction of the large body of professional chemists, to protect whose interests the Institute was founded.—I am, &c.,

CHARLES E. GROVES.

Guy's Hospital, London,
February 8, 1892.

THE DENSITIES OF SULPHURIC ACID.

To the Editor of the Chemical News.

SIR,—Owing to my not asking for a revise of my paper in CHEM. NEWS, vol. lxx., p. 13, a few errata have remained, as "leader" in lieu of "teacher," (p. 13) and "lowest" freezing point in lieu of "highest" (p. 14). The latter is so obviously a slip of the pen that nobody but Professor Pickering would have construed it as a "misrepresentation" as he does in his letter at p. 50. His letter, in which he does not even retract the charge of wilful misrepresentation, puts him more than ever out of court for any further discussion in the columns of a scientific journal. I have only to add that any reader of No. 1676 will discover more than one reason why Prof. Pickering's assertion of having attained an actual accuracy of 0.01 per cent in his sulphuric acid tables is utterly untenable. I for my part have done with him.—I am, &c.,

GEORGE LUNGE.

Zürich, January 27, 1892.

OBITUARY.

THE LATE DR. A. J. BERNAYS.

THE death of Dr. Bernays, which was announced in the *Times* of January 9th last, removed from our midst one whose loss is very sincerely mourned by those who had the privilege of his acquaintance. Dr. Bernays was a lucid lecturer and a capital experimentalist; and the rare combination of tact and urbanity with which his lectures were delivered gained him the respect of, and gave him a remarkable influence over, the rawest and most unruly "first year's man." Dr. Bernays began his professional career as a lecturer on chemistry and analyst in the town of Derby, and was lecturer at St. Mary's Hospital, Paddington, prior to his appointment to the chair of chemistry at St. Thomas's Hospital, which he occupied for the long period of thirty-one years. He also held some important analytical appointments, and wrote several works on chemistry, among them the very complete, yet concise, "Notes on Analytical Chemistry." Dr. Bernays had, in addition, been Examiner in Chemistry to the Colleges of Physicians and Surgeons. In private life his charming manners and

old-fashioned courtesy endeared him to all who knew him; and it can be truly said that, in addition to being an excellent chemist and an amiable teacher, he was a good man in every sense of the word.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 4, January 25, 1892.

Report on the Deplastering of Wines.—The commission named to examine the question (MM. Berthelot, Gautier, and Duclaux), proposes to reply to the inquiry of the Syndical Chamber of the Wine and Spirit Trade, that the Academy cannot give its approval to the use of strontium salts for deplastering wines, and that it condemns this practice.

The Determination of Molybdenum.—E. Péchard.—This paper will be inserted in full.

The Stereochemistry of Diacetyl Tartaric Acid.—Albert Colson.—The author holds that the notation based on the properties of the regular tetrahedron is insufficient for the representation of the active bodies, and may lead to incorrect provisions.

On Certain Soluble Colouring-Matters Produced by Bacteria in Medical Distilled Waters.—L. Viron.—This paper will also be inserted in full.

On the Occurrence of Phenomena of Nitrification in Media Rich in Organic Matter and having an Acid Reaction.—E. Chuard.—The existence of relatively active nitrification in peat-mould (turf mull) is not without agricultural importance. It is merely necessary to dig up some time beforehand the peat earth, to break it up, and store it in heaps as permeable as possible, but secure from rain in order to have a manure rich in active ammonia.

Ammonia in Rain-Water and in the Atmosphere.—A. Muntz.—In opposition to Albert Lévy the author adheres to his results and those of M. Marcano on the richness of rain-water in ammonia in tropical countries.

MISCELLANEOUS.

The Journal of Inorganic Chemistry.—It is a matter of complaint that communications on inorganic chemistry are at present to be met with scattered through a great number of journals and transactions, where they appear almost as aliens amidst the constantly increasing host of researches on the chemistry of the carbon compounds. This circumstance greatly retards and discourages the study of the other elements, and consequently prevents the harmonious development of the science as a whole. We must remember that, especially since the establishment of the periodic system, inorganic chemistry can no longer be regarded as a merely descriptive science, just as it has been the case with zoology and botany since the promulgation of the doctrine of evolution. Hence a journal is about appearing under the editorship of Prof. Gerhard Krüss, of Munich. Here will be brought forward besides inorganic researches theoretical memoirs in so far as they touch the field of inorganic chemistry, analytical investigations, brief abstracts of papers on inorganic, analytical, and physical chemistry, so that every advance made in the entire scope of inorganic chemistry may here be traced by the reader. The journal will include among its co-operators Berthelot, Blomstrand,

Brauner, Clarke, Classen, Cleve, Cooke, Cossa, Crookes, Ditte, Friedheim, Gibbs, Hempel, Joergensen, Kraut, Lunge, Mallet, Mauro, Mendeleeff, Meyer, Mond, Nilson, Piccini, Roscoe, Seubert, Spring, Thorpe, Winkler, and other colleagues. The journal will be published by Leopold Voss, Hamburg, Hohe Bleichen, 18.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Platinum.—Will any reader conversant with the facts kindly answer the following?—(1) The reason of the recent high price of platinum; (2) The reason of the sudden fall in price; (3) Is there any ground for supposing such a violent fluctuation will occur again within any reasonable time?—M. A. S.

MEETINGS FOR THE WEEK.

- MONDAY, 15th.—Medical, 8.30.
— Society of Arts, 8. "Developments of Electrical Distribution," by Prof. George Forbes, F.R.S.
TUESDAY, 16th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "The Forthcoming Exhibition at Kimberley, South Africa," by Mr. Lewis Atkinson.
WEDNESDAY, 17th.—Society of Arts, 8. "The Pamirs," by Capt. F. E. Younghusband.
— Meteorological, 7.
— Microscopical, 8.
THURSDAY, 18th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Some Recent Biological Discoveries," by Prof. E. Ray Lankester, M.A.
— Institute of Electrical Engineers, 8.
— Chemical, 8. Ballot for the Election of Fellows.
"A Search for a Cellulose Dissolving (Cytolytic) Enzyme in the Digestive Tract of Certain Grain-feeding Animals," by Horace T. Brown, F.R.S. "Limetbin," by Prof. Tilden, F.R.S.
FRIDAY, 19th.—Royal Institution, 9. "On Micro-organisms in their Relation to Chemical Change," by Professor Percy F. Frankland, F.R.S.
— Geological, 3. (Anniversary).
— Queckett Club, 8. (Anniversary).
SATURDAY, 20th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

STANDARD CHEMICAL BOOKS.

Regularly kept in Stock, and sent Carriage Paid.

- Journal of the Chemical Society, 1863 to 1889, 41 vols. cloth, £20.
Ditto 1878 to 1888, complete, 22 vols., £8 8s.
Proceedings of the Royal Society of London, COMPLETE SET from 1854 to 1889; 39 vols., 8vo. cloth. Scarce, £10 10s.
Nature; complete set 1869 to 1888; 39 vols. cloth, £8 8s.
Chemical News, COMPLETE SET, 1860 to 1889; 60 vols. cl., £20.
Chemistry applied to Arts and Manufactures by writers of eminence (Schorlemmer and others); engravings, 8 vols. (1880), £4, for 45s.
Gmelin's Handbook of Chemistry (Organic and Inorganic), by H. WATTS, complete set, 19 vols. cl., scarce, £20, for £7 17s. 6d.
Watts' Dicty. of Chemistry and the Allied Sciences; complete set UNABRIDGED EDITION, 9 vols. cloth, 1863-81, £15 2s., for £7 7s.
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N.B.—The Plant and Machinery forming the contents of the above works will be Sold piecemeal by Public Auction the day following the sale of the premises; vide Advertisements.

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WEDNESDAY, 17th, and THURSDAY, 18th FEBRUARY, 1892.

Re L. COWAN AND SONS, Hammersmith Bridge Sugar Refinery, Barnes, London, S.W.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1682.

NOTE ON THE CONDUCTIVITY OF PEROXIDE OF LEAD.

By JOHN SHIELDS, Ph.D., B.Sc.

WHEN a solution of sodium lead tartrate is electrolysed, hydrated peroxide of lead separates out on the positive electrode. The formula ascribed to this peroxide by Wernicke and Streintz is H_2PbO_3 , and a sample which I analysed contained:—

	Found.	Theory.
PbO_2	93.46	93.0
H_2O	6.54	7.0
	100.00	100.00

which corresponds sufficiently well with the theory.

In order to decide whether peroxide of lead and its hydrate conduct electricity like the metals or like electrolytes, pure peroxide was prepared by Wöhler's method (*Fourn. fur Prakt. Chemie*, vol. xc., p. 383), whilst the hydrate was deposited electrolytically from a solution of sodium lead tartrate on a sheet of platinum. The hydrate was washed thoroughly with water, alcohol, and ether, and allowed to lie in the air until its weight remained constant, when it possessed the composition given above.

The first method employed was the following. The chemically and electrolytically prepared peroxides were pressed into circular discs 13.3 m.m. in diameter, which were then firmly clamped between two platinum plates connected with a battery. After the current had passed for a considerable time the battery circuit was broken and at the same moment the plates were placed in connection with a sensitive galvanometer. Although the experiments were repeated several times, no deflection of the galvanometer could be observed. Now, if either of the peroxides conducted electrolytically, decomposition would have ensued on passing the current of electricity, and consequently a polarisation current would have been obtained on breaking the battery circuit and connecting with the galvanometer. As neither of the peroxides gave such a current we must conclude that both conduct electricity metallically.

The result stands in direct opposition to that of Streintz (*Wied. Ann.*, xli., 104), who found that chemically prepared peroxide of lead conducted like a metal, whilst the hydrated peroxide behaved like an electrolyte. I therefore determined to repeat the experiments using another method, namely, that employed by Streintz. Fig. 1 is a diagram of the arrangement. A glass tube, A, is closed at one end with a piece of clean metallic lead or platinum as the case may be, and into the tube is pressed the substance to be examined. This is connected with dilute sulphuric acid contained in the beaker, B, by means of a moist cotton thread. In the beaker stands a rod of amalgamated zinc. The difference of potential between the zinc and the lead or platinum is measured with the electrometer, E (in this case Ostwald's form of the capillary electrometer was used, and the potential difference obtained by compensation).

Now, if the substance contained in A conducts like a metal, we may replace the lead by platinum or any other metal, and the potential difference will always remain the same. On the other hand, if the substance in A is an electrolyte, we will obtain a certain difference of potential between zinc and lead, and if we substitute platinum for lead we will obtain another potential difference, and so on for all the different metals.

I found it convenient to prepare several tubes, half of

which were closed at one end with freshly-scraped lead, and the other half with platinum. The following results were obtained:—

Chemically prepared Peroxide of Lead.

Potential difference Zn—Pb	2.13 Volt.
" " Zn—Pt	2.14 "

Electrolytically prepared Peroxide of Lead (Hydrate).

I.

Potential difference Zn—Pb	2.01 Volt.
" " Zn—Pt	2.02 "

This sample was thoroughly washed with distilled water and dried in the air.

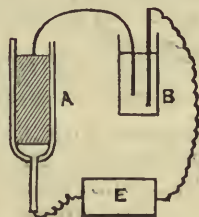
These experiments confirm the result obtained by the first method, and as this does not agree with the observations of Streintz, a fresh quantity of peroxide was prepared electrolytically; it was washed with water, alcohol, and ether, and then at once pressed into the tubes and the measurements made.

Electrolytically prepared Peroxide of Lead (Hydrate).

II.

Potential difference Zn—Pb	1.92 Volt.
" " Zn—Pt	1.94 "

The potential differences observed are in all cases independent of the metal in direct contact with the substance examined, and therefore we must conclude that peroxide of lead, PbO_2 , as well as its hydrate, H_2PbO_3 , conduct electricity in the same way as the metals.



Opportunity was also taken to make an approximate determination of the resistance of the peroxide of lead, and no change in this was noticed on heating to 115° C.

	C.G.S. Units.
Specific resistance of the chemically prepared peroxide	5.59×10^9
Specific resistance of the electrolytically prepared peroxide	6.78×10^9

Leipzig, December, 1891.

AN IMPROVED FORM OF INDUCTION COIL FOR SPECTROSCOPIC WORK.

By H. N. WARREN, Research Analyst.

THE original construction of induction coils known as the continuous wind, constituting what is known as the secondary coil, has been of late superseded by what is termed the segment wind, differing both as regards its insulation and also in its effects when compared with the former system. The following description of a machine of this construction will afford a brief idea of the benefits derived over other systems, when every advantage is taken in manufacturing an article of this description to avoid, if possible, the use of impure elements:—

In this case the primary core was prepared by precipitating pure oxide of iron, igniting, and reducing it in a current of hydrogen gas; afterwards, fusing and forging

the same. Of this substance, 10 lbs. of wire, about the thickness of a wax match and a foot and a half in length, was selected, a pure iron rod composed of the same substance also passing through the centre. This core was covered with several layers of paraffined silk, over which was wound 4 lbs. of very thick insulated copper wire, each layer being carefully insulated; the whole being enclosed, save the extremities, in a thick ebonite tube. Upon this was mounted the secondary, consisting of 25 lbs. of No. 22 double silk-covered wire; on the whole this may be regarded as a thick wire, but the strength afforded, both as regards the spark obtained and also the amount of current allowed, was well merited. The secondary was composed of 52 segments, each separated from each other by mica plates; the whole being coated with paraffin to about two inches in depth, being further cased in ebonite. To the contact-breaker of the machine, in order to absorb the spark, was connected 500 sheets of copper foil, each being insulated by paraffined silk and protected in the usual manner. The machine, as now constructed, required five Bunsen quarts to urge it to its full. The spark thus obtained, which was nearly fifteen inches in length, was the most intense I have ever seen. In some instances, the sudden discharge was equivalent to the report of a rifle, affording a constant stream of thick fire resembling lightning. The supply of ozone liberated was very considerable, almost immediately bleaching cotton fabrics when brought near the same in a moist condition; two dozen large vacuum tubes, two feet long and upwards, were instantaneously lighted; and deal boards, to the thickness of half an inch, were readily pierced; almost every elementary substance was speedily volatilised when brought in contact with the spark, and their spectra thus revealed by the aid of that instrument.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON CERTAIN SOLUBLE COLOURING MATTERS PRODUCED BY BACTERIA IN MEDICINAL DISTILLED WATERS.

By L. VIRON.

In a previous investigation on the part played by Schizomycetes in the coloured reactions which occur in distilled waters (*Journ. Pharm. Chemie*, 1891), we have shown that sometimes the colouration is due to zoogloeic masses suspended in the liquid (as M. Barnouvin states), but that sometimes the colouring-matter is really in solution, since the liquid traversed a Chamberland filter without a decrease of the colouring intensity.

We have been able to isolate some of these pigments in solution; we have succeeded in characterising them chemically, and in cultivating the micro-organisms which produce these colouring principles.

Our first researches were directed to an orange-flower water having a very deep green colour; on evaporation it left 70 m.grms. per cent of fixed residue,—the residue consisting of 69 m.grms. organic matter and 1 m.grm. of mineral substances. The organic matter takes the form of greenish masses, insoluble in ether, chloroform, and benzene; completely soluble in ammoniacal water or on ammoniacal ethero-alcoholic liquid (Adams's galactimetric liquid); soluble in part only in methylic alcohol; but none of these treatments yield the pigment in a crystalline state.

Under the microscope it takes the form of greenish granulations, of rods more or less elongated, and of yellowish lamellae. From this pigment we have been enabled to isolate three distinct colouring matters, and to characterise them by chemical reagents. One of these matters has been isolated by means of methylic alcohol; it is soluble in water, to which it communicates a slight violet tint, which rapidly turns brown in the air. It is

without action on the sulphocarbolic reagent (prepared by dissolving 15 centigrams of carbazol in 100 grms. of pure sulphuric acid), but in contact with nitric and hydrochloric acids it takes a red tint, as does the particular principle detected by Ader in orange-flower water; Ader's principle, however, is volatile, whilst the present pigment is fixed.

The second colouring-matter dissolves in concentrated alcohol with a yellow colour; it is not affected by nitric or hydrochloric acid, but if treated with the sulphocarbazotic reagent there appears a violet-blue colouration and then an indigo-blue precipitate.

The third pigment which we have isolated is insoluble in ethylic and methylic alcohol; it is soluble in water, to which it communicates a fine green tint. It is not affected by the acids nor by the sulphocarbazotic reagent. We have sought what may be the origin of these pigments; were they due to a transformation of principles pre-existing in natural water, or were they a secretion of living organisms? The latter hypothesis alone was verified, the distilled waters, if sterilised by Tyndall's process, having undergone no alteration, whilst check-specimens became coloured more or less strongly.

Cultures of these waters upon plates, according to Koch's procedure in various nutrient media, enabled us to isolate some chromogenic colonies.

These colonies developed the colouring-matter in certain solid media; in some liquid media they multiplied actively, but without producing chromogenic substances.

A mixture of very old distilled lettuce-water and of orange-flower water, previously sterilised, constitutes a medium in which several colonies have secreted pigment.

One of the colonies which have been cultivated gives a brownish pigment which, with hydrochloric and nitric acid, takes a reddish yellow tint, like the pigment obtained from green orange-flower water. We are inclined to consider it as a variety of Schrötter's *Micrococcus cyaneus*. The second colony which we propose to name, *Bacillus aurantii*, appears in the form of elongated cellules, grouped two by two; it is therefore a diplococcus. We have been able to cultivate it in the liquid mentioned above, to which a small quantity of asparagine had been added.

It may also develop itself in certain spoiled distilled waters; we may extract from these liquids a yellow matter, very soluble in water; its solubility has been proved by the Chamberland filter.

The pigment is precipitated from its solution by gelatinous alumina and various other reagents; it is soluble in ethylic alcohol, insoluble in methylic alcohol, and is little affected by luminous rays. To recall its origin we propose to name it *aurantio-luteine*.

The third colony contains small rods which communicate to gelatin a tint yellow by transmitted light and green by reflection. The green tint is especially manifest at the surface. The pigment dissolves in water, to which it imparts a very intense green colour. It is rather rapidly acted upon by luminous rays; it then loses its solubility; it deposits as a blackish mass, and the water becomes colourless. We purpose designating this pigment as *aurantio-chlorine*.

Lastly, a further colony has been isolated and studied. It is met in waters which are much decomposed. It liquefies gelatin, communicating to it a greenish yellow fluorescent tint. It approximates to *Bacillus fluorescens liquefaciens*.

The liquids containing these various pigments are harmless if injected into animals after sterilisation. Only the liquid, in which the last bacillus mentioned above is active, for if injected into guinea-pigs it determines a very intense inflammatory reaction and the animal ordinarily dies after a few days.

This bacillus, therefore, gives rise to a phlogogenous principle approximating to the secretion of certain pathogenic microbes described by Arloing.

These small organisms are quickly exhausted. After

two or three sowings in media which are sparingly nutritive the chromogenic properties disappear, but they reappear if the microphytes are caused to develop in stronger nutrient media.

Sometimes the chromogenic principle seems non-existent, but suddenly the liquid takes a very decided tint if we agitate it in contact with the air, or if we slightly modify its reaction.—*Comptes Rendus*, cxiv., 179.

ON THE DETERMINATION OF MOLYBDENUM.

By E. PÉCHARD.

THE determination of molybdenum in the molybdates is generally effected by precipitating it in the state of sulphide, but the method gives uncertain results, on account of the difficulty encountered in weighing this sulphide. The separation and determination of molybdic acid are effected, on the contrary, without difficulty, by means of the following process.

If we pass in the cold a current of hydrochloric acid gas over an alkaline molybdate the salt becomes yellow. If we raise the temperature we see long white needles being deposited in the tube in which we operate, as observed by H. Debray (*Comptes Rendus*, vol. xlii.), on causing hydrochloric acid to pass over molybdic acid heated to 200°. If we operate upon an alkaline molybdate heated to 440°, the separation of the acid and the base is complete, and the latter remains entirely as a chloride in the boat which contained the salt to be analysed. The white needles obtained in this operation, the composition of which has been established by H. Debray, have the formula $\text{MoO}_3\cdot 2\text{HCl}$. They are very soluble in water, and their solution, if submitted to evaporation at 100°, is decomposed, evolving hydrochloric acid, and leaving a white residue of molybdic acid, which may be at once weighed in the vessel in which the evaporation has been effected.

On operating as just described we always find a slight bluish coating deposited in the tube; it is volatile and insoluble in water. This compound is due to a partial reduction of molybdic acid, and dissolves readily on adding nitric acid to the water which serves to rinse out the tube.

This method, more easily used than the other procedures for determining molybdenum gives excellent results. It cannot be applied to ammoniacal molybdates, but their analysis is very simple. I have ascertained, in fact, that it is sufficient to heat ammonium molybdate to 440° in order to expel all the base.

Weights of ammonium molybdate equal to 2.4217 grms., and 1.5251 grms. have respectively given 1.9003 and 1.1962 grms. of molybdic acid free from ammonia. These two numbers correspond to the same proportion, 78.4 per cent of the weight of the salt taken.

In my analyses I have always taken care to attack the molybdate with hydrochloric acid at the fixed temperature of 440° to avoid the volatilisation of alkaline chloride. The molybdic hydrochlorate does not necessitate so high a temperature for its formation; it is produced in the cold, as I have been able to prove by exhausting with ether an alkaline molybdate, over which I had passed hydrochloric acid in the cold. On evaporation the ethereal solution deposits white crystals identical with those obtained by evaporating a solution of molybdic chlorhydrazine in ether.

These crystals, formed by the combination of molybdic chlorhydrazine and ether, may also be obtained very easily on exhausting with ether a mixture of concentrated hydrochloric acid and a solution of an alkaline molybdate. On evaporation the ethereal liquid deposits fine colourless crystals of the compound above mentioned.

We see, therefore, that, thanks to the production of the

volatile compound $\text{MoO}_3\cdot 2\text{HCl}$, it is easy to effect an accurate analysis of the molybdates. The tungstates, too, not presenting this property, the same method is applicable to the separation of molybdic and tungstic acids in a mixture of their salts. If we cause to pass hydrochloric acid at 440° over a mixture of neutral sodium tungstate and molybdate containing 0.4664 grm. of molybdic acid, this acid is volatilised, and its weight is found = 0.4659 grm.—*Comptes Rendus*, cxiv., 173.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

(Continued from p. 79).

AT one of the last meetings of the Chemical Manure Manufacturers' Association, the following exceptions were taken to the original Glaser method and the following modification adopted (H. H. B. Shepherd, *CHEM. NEWS*, vol. lxiii., p. 251):—

Exception Made.—(a) To working upon a solution representing so little as 0.4 grm. of phosphate.

(b) To employing nitro-hydrochloric acid as a solvent for the raw phosphate, and consequently including in the oxides of iron and aluminum any iron present in the form of pyrites.

(c) To the plan of dividing the phosphate of iron and aluminum found by two, to obtain the oxides instead of determining the phosphoric acid in the precipitate, and deducting this from the total.

Modified Method.—2.5 grms. of the phosphate are dissolved in 10 c.c. of hydrochloric acid and evaporated to dryness, taken up with hydrochloric acid, raised to the boiling point, washed into a 250 c.c. flask with as little water as possible, 10 c.c. of strong sulphuric acid added, and the solution allowed to stand for about five minutes with frequent shaking.

Some 95 per cent alcohol is now added, the mixture cooled, made up to the mark with alcohol, and well shaken. Owing to the contraction in volume which takes place, it must again be made up to the mark and mixed. It is now allowed to stand for one hour, filtered, 200 c.c. of the filtrate taken and gently evaporated to a small bulk in a dish. It is desirable when organic matter is present to carry the evaporation to pastiness, so that the acid may effect its partial destruction. It is then washed into a beaker with about 50 to 100 c.c. of water, boiled for a short time with a few drops of bromine or some other oxidising agent, ammonia added in excess, again boiled for half an hour, cooled, a little more ammonia added to make sure that a slight excess is present, filtered, washed with a hot solution of ammonium chloride, ignited, and weighed. Unless ammonium chloride is present, the precipitate is very apt to wash through even a very close filter. When the weight of the phosphates has been obtained, the precipitate is re-dissolved, and the phosphoric acid in it determined, the amount so found, deducted from the total weight, giving the oxides by difference. Of course, if the oxide of iron is required apart from the alumina, a separate iron determination must be made.

The following postscript was suggested by Messrs. Teschemacher and Smith:—

Should the phosphate under examination contain any magnesia, the phosphates of iron and alumina obtained in the foregoing process must be freed from this impurity by washing the precipitate from the filter and boiling with water and a little nitrate of ammonia, repeating this treatment if after first application the filtrate still shows any magnesia.

Dr. J. H. Vogel (*Zeit. f. Angew. Chem.*, 1891, xii., p.

* Read before the Washington Chemical Society, Nov. 12, 1891, from the *Journal of Analytical and Applied Chemistry*, Vol. v. No. 12.

357) reports series of experiments made by him on the estimation of calcium by Jones's method, and on the presence of magnesia in the precipitate.

With regard to the former, he concludes that the calcium is precipitated quantitatively as sulphate, and as to the latter, he makes the following statement:—

1. That when only small amounts of magnesia are present, it all passes quantitatively into the ammoniacal filtrate.

2. That with Glaser's method, as much as 3 to 3.5 per cent magnesia, and with Jones's modified method as much as 1.5 per cent may be present, there being no danger of its being precipitated with the iron and aluminum as long as care is taken to remove all the free ammonia by boiling.

3. That after the magnesia has come down with the phosphates, it will not re-dissolve on boiling, magnesium-ammonium phosphate being only sparingly soluble in hot water.

The same author has also proposed to combine the Glaser and Stutzer methods (the latter as modified by himself). If the lime is to be estimated, he advises the use of Jones's method. The alcohol is expelled from the filtrate from the calcium sulphate, the phosphates of iron and aluminum precipitated and then analysed by the modified Stutzer method. In the filtrate from the phosphates the magnesia may be thrown down by adding an excess of ammonia and allowing it to stand over night.

As I stated before, the conventional method is an unreliable one, and undoubtedly the alcohol method is a great improvement, as it has never failed to give concordant and, therefore, comparative results as applied to ordinary phosphate rocks in the hands of different chemists. Thus, where simply an approximation of the amount of iron and alumina is desired, it is of great value, the errors involved remaining very nearly constant. But when accurate work is desired, it has, as proposed, few advantages over the old method, one of the strongest objections being that of the Chemical Manure Manufacturers' Association with regard to dividing the total weights of phosphates by two, calling one-half the sum of the ferric and aluminic oxides. To eliminate the error thus introduced, we must make a phosphoric acid determination in the precipitate, and the method becomes long and tedious.

Considering the ease and rapidity with which accurate results are obtained by the molybdate method as I used it, I would prefer the latter at all times. During my work I tried the Glaser method, its modification by Jones, the combined Jones-Stutzer method as proposed by Vogel, and the molybdate method as used by Mr. McElroy.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

February 4th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

Mr. George German was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Meredith Wynter Blyth, 17, Marlborough Hill, N.W.; Reginald Busby Brown, Ellerslie, Knighton Park Road, Leicester; Arthur Carey, Gateacre, near Liverpool; Haridas Garjari, M.A., Agra College, Agra, India; Ernest E. Milnes, Ashfield, Bradford; Arthur Trobridge, Langley, near Birmingham.

Of the following papers those marked * were read:—

*103. "*Pedetic Motion in Relation to Colloidal Solutions.*" By WILLIAM RAMSAY, Ph.D., F.R.S.

Pedetic motion of small particles depends (1) on the size of the particles; (2) on their density; (3) on the nature of the medium in which they are suspended. An electrolyte does not cause the motion to cease at once, but the particles cohere when they happen to touch, and ultimately form clots or clusters. If an electrolyte be not present, the particles do not seem to touch. From observations with the microscope, it is calculated that a particle with a mass of 2.8×10^{-12} grms. moves through approximately its own diameter 1.4×10^{-4} c.m. in a second. Such a particle has one hundred billion times the estimated mass of a water molecule; hence, if its motion be produced by bombardment from water molecules, these must exist in complex groups of considerable mass, and of some stability. It is very unlikely that pedetic motion is the result of electric charges on the particles, because they appear to be uninfluenced by each other's motion; there is no obvious source of such electric potential; and, moreover, we know from Messrs. Linder and Piçon's experiments the result of electrifying them: they are repelled from the positive or negative pole, according to their nature; but their pedetic motion is not interfered with, and is quite different in kind from the flow from the pole. An explanation of this repulsion has been given by Quincke (1861) and by Clausius (1879). The fact that pedesis is stopped by the addition of an electrolyte would appear to show that the water complexes are disintegrated by the presence of ions; it may be that the individual water molecules are attracted by one or other ion, or by both.

The effect of pedetic motion in a liquid is to cause hydrostatic pressure; such hydrostatic pressure would be less on a membrane capable of penetration by the molecular aggregates or particles; and as the suspensions examined by Messrs. Linder and Piçon and the colloids investigated by Graham will not pass through porous clay, they must exert pressure on its surface; the water having fairly free ingress and egress, due probably to the disintegration and the reformation of its molecular complexes.

From actual observation of pedetic motion under the microscope, it cannot be doubted that the relative velocity of two particles depends on their mass; and if their volumes are approximately equal, the less dense particle moves much more actively than the more dense. It would appear not in the least unlikely that equal numbers of equally sized particles would exert equal pressure, as in the case of gases.

In an article by Lothar Meyer (*Kgl. preuss. Akad. d. Wissensch.*, 1892, 26th November), on osmotic pressure, he points out the great discrepancy observed between all measurements of osmotic pressure (except those of Pfeffer on sugar), and the pressure calculated on the supposition that the space was filled with a gas at the same temperature; in all cases the observed osmotic pressure is too low, if it be supposed that ionisation occurs. There are three possibilities: (1) the so-called semi-permeable membrane acts as a sieve, and is quite impermeable to molecules over a certain volume; (2) the membrane is not impermeable, but allows molecules of different momenta to pass at different rates, as with gases of different densities and porous clay; and (3) there is combination of the dissolved substance with the membrane walls, transference through and dissociation of the compound at the interior surface of the walls, as with hydrogen and a palladium diaphragm. Tammann has shown the great probability of the truth of the last hypothesis.

I am disposed to conclude that solution is nothing but subdivision and admixture, owing to attractions between solvent and dissolved substance accompanied by pedetic motion; that the true osmotic pressure has, probably, never been measured; and that a continuous passage can be traced between visible particles in suspension and matter in solution; that, in the words of the old adage, *Natura nihil fit per saltum*.

DISCUSSION.

Mr. J. Y. BUCHANAN, having inquired whether muddy water, such as that flowing from the Rhone into the Lake of Geneva, would exhibit a higher density than the clear water when tested by a hydrometer; and Mr. FRISWELL having said that it was well-known it was impossible to exactly ascertain the density of oil of vitriol containing lead sulphate in suspension by means of a hydrometer, Professor RAMSAY said that as particles in pedetic motion exercise pressure, they necessarily tend to force the hydrometer bulb upwards, and thus cause an apparent increase in the density of the liquid.

Referring to the stoppage of dissolved substances by partly permeable membranes, Mr. HOWARD pointed out that the purification of water by sand filtration had been traced to the formation of growths on the surface of the sand; when these growths reached a certain stage, however, they ceased to act.

*104. "The Acid Action of Drawing-Paper of Different Makes." By W. N. HARTLEY, F.R.S.

In a communication to the British Association, "On the Fading of Water-Colours" (cf. CHEM. NEWS, vol. liv., p. 263), I showed that moisture and acidity were the chief causes of the fading of certain pigments. The acid in the air of towns is produced from sulphur in the coal, in the air of rooms from the excessive amount of gas which is burnt, and in certain colours according to their mode of preparation. It was suggested that even the slight acidity of drawing papers might be expected to facilitate chemical change, the action in each case being a gradual one. I had experimented with various kinds of the best paper in use, both of old and recent manufacture, and had come to the conclusion that such papers were invariably acid, even those of the most excellent quality. The fact was accounted for as follows:—The fibre of which the paper is made is steeped in dilute sulphuric acid, and the subsequent washing with pure water does not entirely remove the acid from linen fibre, of which the best papers are made. I have actually found fine linen to retain traces of acid after it has been steeped in frequently renewed pure distilled water for a period of three weeks. The acid seems to combine with the fibre, and the resulting compound is only slowly decomposed or dissolved by the action of water. Such linen gives a blue colour when an aqueous solution of iodine is dropped upon it. There was no intention to convey the idea that the paper contained free acid in such quantity that it could be easily removed by washing, or that it would affect *litmus paper*, which generally is not a sensitive agent. The samples of paper exhibited at the meeting were carefully tested in the following manner:—A pure and neutral solution of azolitmin, prepared from litmus, was allowed to drop upon the paper and soak into the fibres; the edges of the drops were then examined and found to be red. The bulk of the liquid was then removed by a piece of the same paper, with the result that in every case a red spot was seen which dried red. Another mode of testing was as follows:—A clear sable brush washed in distilled water was used for applying a wash of pure neutral azolitmin solution, as if it were a pigment; such washes turned red upon the paper.

Prof. Church, in his valuable work on "The Chemistry of Paints and Painting," p. 290, published in 1890, remarks that he is unable to endorse my statement that the best drawing papers have an acid action. He finds, in fact, that sized papers are generally neutral to test-papers, and that inferior papers are more often slightly alkaline than acid.

As some doubts may be entertained as to the quality of the papers examined by me, it may be well to state that they were all of the best quality, most of them being of Whatman's make. That no question may arise on this point, I have tested the samples named below in three ways: first, by dropping litmus solution upon the paper; secondly, by washing with a sable brush; thirdly,

by steeping strips of paper in pure distilled warm water, and testing the water for acidity, and also for sulphates. The acid action was recognised by a pure litmus solution, by an ordinary laboratory preparation, and by a carefully prepared solution of helianthin, though this last agent is not very sensitive.

The results are identical with such as I obtained on former occasions. The description of the samples and their actions is as follows:—

1. Whatman's hand-made paper, 96 lbs., old make. Washes, acid; drops, acid; water, decidedly acid. Large precipitate with barium sulphate insoluble in dilute chlorhydric acid.

2. Whatman's double thick imperial, 140 lbs. Washes, acid; drops, acid; water, decidedly acid. Large precipitate of barium sulphate, as with No. 1.

3. Whatman's double elephant, hand-made. Washes, acid; drops, acid; water, strongly acid. Large precipitate of barium sulphate, as with No. 1.

4. Whatman's hand-made, 72 lbs., 1887. Washes, acid; drops, acid; water, decidedly acid. Large precipitate of barium sulphate, as with No. 1.

5. Saunders's hand-made. Washes, acid; drops, acid; water, decidedly acid.

6. Hollingworth's machine-made paper. Washes, barely acid; drops of strong litmus neutral in colour; water, very slightly acid, almost neutral.

7. Arnold's unbleached hand-made paper. Washes, acid.

No further tests for acidity were recorded.

All these samples were procured from Mr. Spence, Lower Sackville Street, Dublin, especially for the purpose of these tests. It will be seen from these notes that there were good grounds for attributing an acid action to even the best of drawing papers. In other words, if a very sensitive solution of pure litmus be applied to paper in the same manner as a strong pigment, as, for instance, in delicate washes, the action is, in almost every case, distinctly acid; but if a drop of a strong solution be allowed to sink into the paper and dry up, its colour may be so slightly changed as to appear violet, leading to the inference that the paper is neutral. The strength of the solution of litmus, and the manner in which it is applied, must therefore be taken into account, because the quantity of the purple colouring matter in contact with the paper may be more than sufficient to overpower the red tint caused by the acid present in the moistened material. It is therefore extremely probable that there has been no difference between the opinions of Professor Church and myself, but only an incomplete understanding as to the degree of acidity of the paper. Solutions of helianthin painted on the various samples of paper gave at first a pure yellow tint, which gradually changed to a colour intermediate between rose colour and yellow. Very dilute solutions, washed on freely, showed after some minutes a pale rose colour, mixed with a yellowish tinge.

A sufficiency of acid yields a fine rose tint with such a solution. Hollingworth's paper did not show in any degree an acid action with helianthin, although it gave a slight indication with litmus.

DISCUSSION.

Mr. WADE remarked that perhaps the sulphate detected by Professor Hartley was derived from thiosulphate, which, it was well known, was used as an antichlor in manufacturing paper.

Mr. GROVES said it would be desirable to know more of the history of the papers. Was gas burnt in the room in which they were stored, and were the sheets examined taken from the tops of the packets? If so, it was possible that the sulphuric acid was derived from the gas; it would be desirable to test the centre portions of sheets taken from the middle of the packet.

Professor HARTLEY's remarks on this criticism are as follows:—The circumstances are not within my recollection, and I am unable to make enquiry at present, but

drawing paper in sheets is kept in drawers, at a height of not more than three or four feet from the ground, and carefully protected from dust and damp. As a rule, the samples tested by me have been taken from the middle sheets of sketch blocks prepared from Whatman's hand-made papers, and purchased from Lechertier, Barbe, and Co., Regent Street. Imperial and double elephant were the kinds most used. I am well acquainted with the effect of a sulphurous atmosphere on paper, but cannot think that the acidity to which I refer is to be attributed to such a cause.

105. "*The Interactions Occurring in Flames.*" A Correspondence between Sir G. G. STOKES, Bart., F.R.S., and HENRY E. ARMSTRONG.

The following correspondence will serve as a contribution to the recent discussion of the chemistry of flames brought under the notice of the Society by Professor Smithells and Mr. Ingle, and by Professor Lewes. The paper referred to by Sir G. G. Stokes is entitled "On an Optical Proof of the Existence of Suspended Matter in Flames" (*cf. Proc. Roy. Soc. Edin.*, 1891). It was reproduced in *Nature*, xlv., 263, 1891.

"4, Windsor Terrace, Malahide, Ireland,
September 23, 1891.

DEAR DR. ARMSTRONG,—I enclose a little optico-chemical paper, that is to say, one in which the method is optical, but the results are of interest, such as they have, rather from a chemical point of view. I use, to express it in short terms, a flame as a screen on which to receive an image of the sun.

The reaction mentioned in the P.S. is to be taken as a specimen of reactions of the kind, for though it probably takes place, there are doubtless others also, as there are a lot of compounds found in the interior of the flame.

I read the other day your address to the Junior Engineering Society, in which you speak of oxygen combining with hydrogen in preference to carbon; I should have supposed it would have been the other way. Not only does the facility with which steam is decomposed by glowing carbon favour this view, but it seems to me to fit better with the phenomena of flames. According to my notions, we must carefully distinguish between the changes which take place in the partial combustion of a molecule and those which are produced in neighbouring molecules as a result of the heat thus produced. We may, for the sake of a name, call the former pure chemical, and the latter thermo-chemical. The action of the heated walls of a tube is of the thermo-chemical kind; it involves a re-grouping of the existing molecules under the molecular agitation of a hot body, without bringing a fresh reagent (suppose oxygen) into play from outside the molecule. I think that in the blue base of the flame of a candle, where oxygen is plentiful, we have pure-chemical changes. The blue shell invests for a little way the highly luminous shell, like a calyx investing a corolla, and I think the thin shell of glowing carbon, to which the bulk of the light is due, owes its origin to a thermo-chemical change, the heat being derived from the combinations with oxygen which take place just outside it.

I imagine that the hydrocarbon spectrum is due to a gas formed by a pure-chemical as distinguished from a thermo-chemical change. But what gas is it? It is commonly supposed to be acetylene. To me it seems more probable that it is marsh gas, formed by a pure-chemical, not a thermo-chemical, change. According to my notion, this unknown gas (x , say) is a hydrocarbon, which when burnt without admixture of other hydrocarbons would show but feebly, if at all, the hydrocarbon spectrum. More especially might this be expected to take place if it were burnt at a reduced pressure, or considerably diluted with, say, nitrogen. For in order that x should show its spectrum its molecule must be in a state of violent agitation, which it might be expected to be if it had been born as a result of partial combustion, but would not be merely because it was going to be slain by union with oxygen.

I have not seen a statement as to the spectrum of marsh gas, as pure as may be, when burnt. Perhaps you know about it. As hydrocarbons in general (I don't know how it is as to marsh gas) show the same spectrum, x must be some gas of a simple kind formed in the process of partial combustion, though probably (at least under ordinary circumstances) itself burnt almost immediately afterwards.—Yours very truly,

G. G. STOKES."

"January 18, 1892.

DEAR SIR GEORGE STOKES,—The question of the manner in which hydrocarbons are burnt, raised in your letter, has recently (on December 3rd, 1891) been brought under discussion at the Chemical Society by Professor Smithells in two papers dealing with the structure and chemistry of flames; the conclusions at which he arrives are practically identical with yours.

In making (in 1887) the statements to which you refer, I was, to a certain extent, but retailing a not uncommon opinion, although probably I was led to give prominence to the idea that hydrogen is the more combustible constituent of a hydrocarbon by the circumstance that a gas, such as methane, CH_4 , yields acetylene, C_2H_2 , as one of the products of its incomplete combustion; it is possible that this latter may be formed by the agency of heat alone, but I certainly am inclined to regard its production as due to partial removal of the hydrogen from CH_4 , by oxygen, the more so, as Dr. Miller and I were unable to detect acetylene in oil gas manufactured by passing petroleum hydrocarbons through highly heated retorts (*cf. C. S. Trans.*, 1886, 80). Clearly, however, the case is one about which we can only reason at present; a crucial experiment which would afford a solution of the problem will not be easily devised, I think.

At the close of 1886, when my address was written, we were but beginning to realise that the phenomena of combustion are far less simple than had up to that time been taught. Had I spoken of the subject a year or two later, I should undoubtedly have adopted a less dogmatic style. Still, while admitting that the facts do not justify the assertion that oxygen combines with hydrogen in preference to carbon when a hydrocarbon is burnt with insufficient oxygen, I am unprepared at present to accept the alternative view which both you and Professor Smithells advocate, that the carbon is the more combustible; I think the actual condition of affairs is far less simple than is expressed in the statement of either of these views.

In the case of the changes attending combustion you would draw a distinction between "pure chemical" and "thermo-chemical" changes. It is impossible to deny that such a differentiation of the changes is seemingly necessary, but perhaps after all the difference is but superficial.

I cannot help thinking there is very little opportunity in flames for simple heat changes to occur; the molecules of different kinds are so mixed up together. Thus opportunity is given for interactions to occur, the end result of which is the same as that of a simple heat change of the chief substance concerned, merely because a change occurring at one moment is reversed the next, and so escapes notice. In this way contiguous molecules may play the part of surfaces, and that such actions are of primary importance in the case of "decompositions" as well as in the case of "compositions," there can, I think, be little doubt. Thus it appears to be established that a pure mixture of carbonic oxide and oxygen is incombustible; is it not therefore reasonable to suppose that under parallel conditions pure carbon dioxide is unresolvable into carbonic oxide and oxygen? Again, the results of recent experiments by Victor Meyer seem to prove that, as I have long suspected, the formation of water from hydrogen and oxygen is not the simple phenomenon it is represented to be by the simple equation $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$; and conversely it is well known that the extent to which the dissociation of water

takes place depends on the character of the surface in contact, with which it is heated, and not merely on the temperature. In fine, it seems permissible to doubt whether under the conditions prevailing in flames carbon is ever separated by simple heat changes; at all events, there is at present no evidence compelling us to conclude that it is.

Professor Smithells contends that probably carbon has a higher heat of combustion than hydrogen; this may be, but in the absence of all data from which the heats of combustion of atomic carbon and hydrogen can be inferred, we cannot, with safety, base any argument on thermochemical values. But even if it have, it does not follow that carbon is not liberated by partial combustion of hydrocarbons. It is not merely a question of the relative affinities of carbon and hydrogen for oxygen. The carbon would not, I imagine, be atomic carbon, but that complex molecular form which occurs in the flame in the solid state, and being incandescent renders it luminous. The genesis of such carbon is expressible by an equation such as—



Professor Smithells takes no account of the heat evolved in the formation of C_x from $x\text{C}$. I may also point to the superior stability at high temperatures of CO_2 as compared with CO as remarkable, seeing that it is the more complex molecule, especially as there is some ground for the belief that proportionally more heat is evolved in the fixation by carbon of the first than of the second atom of oxygen (*cf. Phil. Mag.*, [5], xxiii., 103, Feb., 1887). The probable explanation, as Berthelot has suggested, is that in this case, also, the decomposition of CO is promoted by the tendency of carbon atoms to combine.

It is also to be remembered that, although carbonic oxide as well as carbon and steam appear to interact readily enough if the temperature be sufficiently high, dry carbonic oxide and carbon do not burn in dry oxygen; nothing better illustrates the difficulty of drawing conclusions in these cases than such facts as these.

There is another point of view from which the phenomena may be regarded, from which it would seem that it is impossible to define either constituent of a hydrocarbon as the more combustible, except in a purely conventional sense. We may liken the interchanges occurring in an oxygen-methane mixture to those that occur in a cell in which two like electrodes are immersed in two different electrolytes—an aluminium acid-alkali cell, such as Wöhler (?) proposed, for example. The oxygen molecule O_2 corresponds to the aluminium, the hydrogen and carbon of the methane to the acid and alkali; and just as the aluminium is attacked in two ways, so the oxygen may conceivably become distributed between the carbon and hydrogen. The formation of the two aluminium compounds is independent of the relative affinity to aluminium of the radicals of the acid and alkali, and in like manner that of the two oxides from methane would be conditioned by the orientation of the oxygen atoms relatively to the carbon and hydrogen atoms of the hydrocarbon; for we may assume, I think, that the colliding oxygen and hydrocarbon molecules conjugate if only during a very brief interval of time, and that interaction is indeed a consequence of the opportunity thus given to the atoms to re-group themselves.

There appears to be no doubt that surfaces of various kinds—I would even include gaseous surfaces—play an all-important part in promoting all kinds of reversible changes; but it is a fair question for discussion whether their action is not also of a "pure chemical" character. The fact that the nature of the surface is of moment is in favour of the view that it is—the surface must be a compatible one: the separation of hydrogen from a hydrogen compound being especially promoted by platinum, which undoubtedly has a strong affinity for hydrogen, and that of oxygen being promoted by silver, which, at high temperatures, is known to absorb this gas. On the other hand, copper, although so readily oxidisable, does not appear to

promote the decomposition of water. Even in such a case as that of the dissociation of carbon dioxide by red hot porcelain, it is conceivable that the porcelain may exert an attraction over atomic oxygen sufficient to induce its separation from carbon. I, therefore, am not satisfied that the action of the heated walls of a tube is, as you suggest, strictly of the thermo-chemical kind.

There is a striking passage in Faraday's paper on the influence of platinum in promoting the interaction of hydrogen and oxygen (*Exp. Res.*, Series VI., paragraph 656, November, 1833), which shows that he had clearly realised how important is the influence of surface action even in the case of flames. He says:—

'I have pursued this subject at some length as one of great consequence, because I am convinced that the superficial actions of matter, whether between two bodies or of one piece of the same body, and the actions of particles not directly or strongly in combination are becoming daily more and more important to our theories of chemical as well as of mechanical philosophy. In all ordinary cases of combustion it is evident that an action of the kind considered, occurring upon the surface of the carbon in the fire, and also in the bright part of a flame, must have great influence over the combination there taking place.'

Regarding the interactions in flames as consisting in a series of simultaneous and consecutive explosions, of which we can only examine the final steady state, it seems to me that the phenomena are necessarily of an excessively complex character, and that their appreciation and successful interpretation must tax our powers of mental analysis in a very high degree. It will certainly be unwise at present to infer that the oxidation of the hydrocarbons, or the separation of carbon and also of hydrogen from them, takes place entirely in any one way.—Yours very truly,

HENRY E. ARMSTRONG."

" 21st January, 1892.

DEAR PROFESSOR ARMSTRONG,—Perhaps I may be allowed to add a few words in explanation of what I meant by thermo-chemical change. I had not in view thermic measurements. I will endeavour to explain my ideas by an example. Let us contrast (a) the formation of water from mixed oxygen and hydrogen, (b) the formation of acetylene and hydrogen from marsh-gas at a high temperature. In both cases alike molecular agitation is required to bring about the change; in (a) if the change be brought about at one point, the consequent agitation supplies the requisite disturbance to the neighbouring molecules, and the change is propagated with explosions; but in (b) I picture to my own mind the change as taking place in this way. When sufficient heat is supplied to the gas from without, the collisions of the molecules of the marsh-gas become sufficiently violent to allow the carbon atoms in a pair to get into a condition in which their tendency to self-combination comes into play, and in the coalescing a portion of the total hydrogen in the pair is thrown off. But the continuance of this change is dependent on a continuous supply of heat from without, under which it is gradually effected. I should call (a) a pure-chemical change, even though heat at one point is necessary to start it, and I should call (b) thermo-chemical, even though chemical affinities are concerned in it.

The results of Prof. Smithells seem to me to make it probable that x may be carbonic oxide.—Yours very truly,

G. G. STOKES."

106. "Properties of Alcoholic and other Solutions of Mercuric and other Chlorides." By S. SKINNER, M.A.

The author has determined the variation in the boiling-point of alcohol produced by dissolving in it mercuric, lithium, magnesium, and calcium chlorides, as well as the variation in the boiling-point of a solution of hydrogen

chloride of constant boiling-point produced by mercuric chloride. He has also studied the distribution of mercuric chloride between the two solvents water and ether.

The results indicate that mercuric chloride affords a case in which the measure of the property is a simple function of the quantity of salt present, whereas in the case of the other chlorides the measure of the property involves some higher power.

107. "*The Isomeric α -Bromocinnamic Acids.*" By S. RUHEMANN, Ph.D., M.A.

An account is given of experiments on the action of ammonia and phenylhydrazine on the ethereal salts of the two isomeric bromo-acids obtained on withdrawal of hydrogen bromide from dibromohydrocinnamic acid. Whereas the ethylic salt of α -bromocinnamic acid and ammonia readily interact, yielding α -bromocinnamamide, the α -isocinnamate is scarcely affected by ammonia.

Both salts are converted by phenylhydrazine into a compound of the formula $C_{15}H_{11}N_3O$, the change taking place less readily in the case of the iso-salt. The author regards this product as cinnamylphenylazimide; the same substance is more readily prepared by interaction of ethylic dibromohydrocinnamate and phenylhydrazine. In both cases the yield of azimide is but small, the main product being a compound of the formula $C_{24}H_{18}N_4O_2$, probably the imide of dicinnamylphenylazimide. The author discusses the manner in which this compound is formed.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—Mr. Groves (CHEM. NEWS, vol. lxx., p. 84) says that the circular issued by the Association of which I am the Honorary Secretary gives a garbled quotation from the Charter, in stating that the Institute was founded for the elevation of "analytical chemists," instead of "consulting and analytical chemists." Mr. Groves has taken an uncharitable view of that omission, for I find on referring to the original copy sent to the printer that the words are correctly quoted; but the printer, unfortunately, omitted the word "consulting," and I had not time to revise the proof as carefully as I should have wished. The omission, however, of the word "consulting" rather detracts than otherwise from the strength of the position taken by the Association.

The Institute was founded for the elevation and regulation of persons in practice as consulting and analytical chemists, and not for those engaged as professors of, or lecturers on, chemistry. It is obvious, however, that we have many brilliant chemists amongst the professors and lecturers, and everyone will agree that the views of those gentlemen should receive the most careful consideration. Chemists engaged in works ought also to have a large measure of influence in the management of the affairs of the Institute. But, according to the Charter, the Institute was founded mainly for the elevation of consulting and analytical chemists, in order to give to them a higher position, by reason of their being recognised as qualified, and the public greater assurance as to their qualifications. Under these circumstances surely the managing body should consist mainly of members who are in active practice as consulting and analytical chemists.

Mr. Groves asserts that no pledge was given to publish a full report of the proceedings of the Conferences of the Institute. Those who were present at the May meeting will no doubt remember that Mr. Groves stated that it was intended to publish full reports for the benefit of members who could not attend the proceedings of the

Conference. Shorthand notes were taken for that purpose, and the transcript of remarks which I made was forwarded to me for correction. This I revised and returned to Mr. Groves, and I was subsequently informed, after the papers and discussions were in print, that the Publication Committee had resolved not to circulate them amongst the members of the Institute. But the circular referring to the December Conference, which Mr. Groves cites, says: "A full report of the proceedings will not be published." Will Mr. Groves say that a report of any kind whatever, either full or otherwise, has been or will be published? And if not, will he say that the pledge that a report of some kind would be published has not been broken?

The chief object of our Association is to obtain better representation on the Council of the Institute by members who are in active practice as consulting and analytical chemists, and I have received many replies from professors of, and lecturers on, chemistry who think this is a fair thing to ask. There is no breach between consulting and analytical chemists on the one hand and teachers of chemistry on the other, so far as I know.

I am sorry Mr. Groves wrote the last paragraph of his letter, because it insinuates sinister motives on the part of gentlemen who, no one could doubt, would fully uphold the integrity and dignity of the Institute.

Mr. Groves requests the members not to hand over the Institute bound hand and foot to the public analysts, "or rather to a small and noisy party of progress (?), who form but an exceedingly small fraction of the large body of professional chemists." It must be evident to Mr. Groves, although we do not make any such assertion, that we might with equal justice say that it at present lies bound hand and foot under the dictation of a small body of lecturers on chemistry, who form a still smaller section of the whole body of the Institute. We have too much respect for all the members nominated on the proposed Council to make such an assertion, and are content to place our views before the Institute, which we have done by a circular addressed to each member, and to leave the decision with them. If they think that members in active practice as consulting and analytical chemists should form at least half the number of the governing body, I trust they will vote for the list we shall propose to them. If they do not hold these views, they will no doubt vote against us, and Mr. Groves will find by the result which views are the more acceptable to members.

It is specially provided by the Charter that alterations in the Council may be made every year by the members, and I trust that Mr. Groves will not try to imbue them with the erroneous notion that they have no moral right to make use of that provision to express their views. If the action of the Council so elected be not pleasing to the majority of the members, the same provision will enable them next year to alter the Council as they think fit. The Council is to the Institute what the House of Commons is to the Nation. The majority of the Council corresponds to the supporters of the Government, and if their policy is distasteful to the general body of members it is strictly within the province of the latter to replace them by men who will better represent their views.—I am, &c.,

WILLIAM THOMSON.

Manchester, Feb. 13, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—As one of the fifty-nine members of the Institute of Chemistry who signed the circular to which Mr. C. E. Groves takes exception in his letter published on p. 84, I desire to say that Mr. Groves is quite right in his belief that neither Mr. W. Thomson, myself, nor any of our co-signatories would have consented to their names being attached to a document which they knew contained

garbled quotations or untrue statements. In fact, the names appended to the circular include those of men in the first rank and all branches of their profession, representing every part of the kingdom. That these gentlemen have formed an association and appealed to their brother chemists to adopt proper constitutional means to effect a change in the management of the affairs of the Institute, is at once a proof that reform is urgently required, and a guarantee that the agitation will be conducted with fairness, frankness, and moderation.

How the words "and consulting" came to be omitted from a sentence purporting to be quoted from the Charter I do not know, but Mr. Groves' suggestion that the omission was designed is clearly untenable. The whole gist of the circular evidently is that the interests of the Institute have suffered and its objects been imperfectly attained through the consulting and analytical chemists in active practice not being adequately represented on the Council; and the policy of the Association is clearly set forth as being to secure the election on the new Council of a majority of those coming under this designation.

As Mr. Groves takes upon himself to correct certain statements in the circular, he should, at least, take care that his own allegations are not open to exception. Thus he describes the fifty-nine signatories as "some fifty members of the Institute, nearly all public analysts," whereas I can only count some fifteen or sixteen (or 25 per cent), as holding public analysts' appointments. Among the remainder I recognise the names of professors and lecturers on chemistry, consulting and analytical chemists, pharmaceutical chemists, works managers and chemists, medical men, &c.

But Mr. Groves is guilty of a still less excusable inaccuracy, and one which, coming from him, somewhat surprises me. He asserts that the statement in the circular that "a distinct pledge was given that the papers and discussions of last year's conferences should be published" is, "to speak quite plainly, untrue." So far from being "untrue," *I myself, with scores of others, heard Mr. Groves state* that the papers and discussions at the May Conference would be published in full. This promise was given by Mr. Groves in open meeting, in reply to a direct question as to the intentions of the Council. Further, a shorthand writer attended and took verbatim notes of the discussions. These were afterwards transcribed, and I duly corrected and returned to Mr. Groves the report of my own share in the discussions.

Proceedings in Council are generally held to be more or less confidential, but it is an open secret, which, I presume, will become generally known on publication of the balance-sheet, that the papers and discussions were duly printed at a cost of upwards of fifty pounds! I did my best to induce the Council to publish the reports of the May Conference, and believe if this had been done it would have furnished a safety-valve for the rapidly growing dissatisfaction with the past policy of the Council, and probably have prevented the present action of the members.

While Mr. Groves gave a definite promise that a full report of the May Conference should be published, it is quite true that it was announced that no full report would be published of the Conference held in Christmas week; which decision was undoubtedly wise, bearing in mind the eminently inconvenient date chosen for the meeting, and the broken pledge respecting the proceedings at the previous Conference.

I may say that personally I greatly regret that such a course as that which members are now taking should have been rendered necessary; but my experience in the Council of the Institute has convinced me that no good can be expected without such a change in its policy as can only be effected by placing on it a working majority of those actively interested in the primary object for which the Institute was founded; which, as defined by the Charter, is "the elevation of the profession of con-

sulting and analytical chemistry, and the promotion of the efficiency and usefulness of persons practising the same, by compelling the observance of strict rules of membership and by setting up a high standard of scientific and practical proficiency." If repeated disappointments had not convinced me of the hopelessness of attempts at reform from within the present and proposed Council, I should not have joined the Association, and in taking that step I am in no way animated by personal feeling or want of good will towards those members of the Council whom I hope the supporters of the Association will succeed in replacing by men more directly representative of those branches of the profession which I hold should constitute the majority.

Whatever may be the divergence in our views, I presume that all are acting in what they believe to be the best interests of the Institute, and hence I deprecate such sneers as those indulged in by Mr. Groves. They merely serve to accentuate the unfortunate differences between the various branches of the profession, while affording to neutral men a clue to the spirit and policy which have brought about the present lamentable condition of things. It is always painful to disagree with one's personal friends, and I am proud to be able to count many of these in every branch of the profession; but I fail to see that the matters at issue justify the adoption of such a tone as that of which Mr. Groves makes himself the mouthpiece.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, February, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The circular against which the wrath of the late Secretary of the Institute of Chemistry is directed was signed by 59 members of the Institute. According to Mr. Groves these are nearly all Public Analysts who are trying to hand over the Institute bound hand and foot to their own body.

As the President of the Society of Public Analysts, I am bound to show that this allegation is entirely unwarranted. Of the 59 signatories only 16 are Consulting and Analytical Chemists holding appointments as Public Analysts. The movement is therefore wrongly designated a Public Analyst movement. It is one of Analytical and Consulting Chemists against the usurpation of their rights, as expressed by the Charter of the Institute, by a certain number of chemists whose interest in the Institute is merely of a secondary character. Mr. Groves should recognise that the majority of those who have signed the circular have as much right to the designation of Consulting Chemist as he himself has.

It is idle to call the party who are now once more attempting to guide the Institute upon the strength of the charter into constitutional lines, "a small and noisy one," "who form but an exceedingly small fraction of the large body of professional chemists." There is an equally noisy fraction among the party that has so long been in power with disastrous results. The ballot at the annual meeting will, I believe, disagreeably surprise the late secretary.

As a late member of Council I desire to add that Mr. Groves must surely know that the conferences of the Institute were started with the full intention on the part of the Council to publish the papers and discussions. The matter was at great length before the Council, and it was well understood that the publication should, if possible, be the means of showing to the Fellows that the Institute was not so inactive and useless as was largely believed. Only when it was found that the discussions and papers were distinctly hostile to the past policy of the Council, and after the papers read and the discussion at the first conference were in type, did the Council alter its former intention and relapse into its policy of silence.

This is fresh in the recollection of many of those who, like myself, were members of the Council at the time the conferences were resolved upon. Whether there is any documentary evidence of the fact is beside the point, for surely Mr. Groves does not intend to distinguish between his word and his bond.—I am, &c.,

OTTO HEHNER.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

SIR,—Some college students have recently formed a scientific society for their general benefit and the furtherance of their chemical knowledge. Now the students have the difficulty (which no doubt you once experienced yourself), in selecting the branch of chemistry they should follow. I am therefore requested to ask for opinions on that subject.

The question then is, should a young chemist take up the teaching of chemistry, or should he take it up with a view to a future position as public analyst? or, again, should he go into a works as an analytical chemist? If the latter, what branch in particular would you recommend to anyone who has a wish for future advancement, and also has some enthusiasm for the science?—I am, &c.,

W. S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 5, February 1, 1892.

Compressibility of Saline Solutions.—Henri Gilbert.—The author has essentially followed the method adopted by Cailliet, and he has formulated twelve laws.

Barium and Strontium Nitrides.—M. Maquenne.—On passing a current of nitrogen at a red heat over an amalgam of barium, strontium, or calcium, placed in a boat of iron and nickel, we obtain a mixture of alkaline-earth nitride with a slight excess of the corresponding metal, particles of finely divided iron or nickel, a little mercury, and lastly a trace of baryta, strontia, or lime. The quantity of hydrogen given off on treating this mixture with water varied greatly. Barium and strontium nitrides have the same constitution as magnesium nitride, $Ba=N-Ba-N=Ba$, which recalls immediately that of triethylene diamine. Barium nitride does not yield ethylated bases with alcohol. At a red heat it fixes energetically carbon monoxide, and is thus converted into a mixture of baryta and barium cyanide. Lithium is also capable of rapidly absorbing nitrogen, thus presenting a new analogy between this metal and those of the magnesium family.

On Carbon Chlorobromides.—A. Besson.—Theory indicates the probable existence of three carbon chlorobromides of the type CX_4 , i.e., CCl_3Br , CCl_2Br_2 , $CClBr_3$. The first mentioned was obtained by Friedel and Silva by the action of bromine upon chloroform at 170° in sealed tubes. The author has tried this reaction at a higher temperature, and has obtained simultaneously all the three chlorobromides.

Action of Metals upon Salts dissolved in Organic Liquids.—Raoul Varet.—Certain metals, capable of precipitating other of their salts dissolved in water, lose this property if for water we substitute certain organic liquids; this difference is due sometimes to the water and some-

times to the action of molecular compounds created by the union of the products present.

Monosodium Mannite.—M. de Forcrand.—A thermochemical paper, not suitable for abstraction.

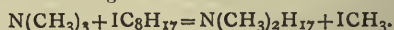
Conversion in the Animal Economy of Sulphanilic Acid into Sulphanilcarbamic Acid.—J. Ville.—Sulphanilic acid, in its passage through the economy, undergoes a modification analogous to that observed by Salkowski in taurine. The acid amine is converted partially into uramic acid and sulphanilcarbamic acid, which is eliminated in urine.

Chemical Study of the Chlorophyllic Substances of the Pericarp of the Grape.—A. Etard.—There exists in the chlorophyllic bodies of the pericarp of the grape a considerable quantity of palmitic acid, partly combined with a substance having a high molecule, and which, doubtless, easily adapts itself to the transformations of organic life on account of the mobility of its properties of hydration.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 11.

Solution of Bismuth Chloride in Saturated Solutions of Ammonium and Sodium Chlorides and on Bismuth Salicylates.—H. Causse.—The author has observed that certain chlorides, especially those of ammonium and sodium, prevent the dissociation of the bismuth and antimony salts by water. He has applied his researches to the preparation of the neutral and the basic bismuth salicylates.

Action of Capryl Iodide upon Trimethylaniline in Aqueous Solutions, Hot, and in Equimolecular Proportions. Formation of Free Dimethylcaprylamine of Tetramethylammonium Iodide, of Trimethylamine Hydriodate, and of Caprylene.—H. and A. Malbot.—The author's results are: dimethylcaprylamine is formed according to the reaction—



Tetramethylammonium iodide results from the union of the trimethylamine which remains available to the methyl iodide formed in the first reaction.

Series 3, Vol. vi., No. 12.

On Codeine Violet.—P. Cazeneuve.—Already noticed.

Determination of Creatinine in Urine.—J. Moitessier.—Already inserted.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Medical, 8.30.

TUESDAY, 23rd.—Royal Institution, 3. "The Brain," by Prof.

Victor Horsley, F.R.S.

Institute of Civil Engineers, 8.

Royal Medical and Chirurgical, 8.30.

Photographic, 8.

Society of Arts, 8. "Artistic Treatment of Jewellery—Jewel and Address Caskets," by Mr. J.

William Tonks.

WEDNESDAY, 24th.—Society of Arts, 8. "Ancient and Modern Art Pottery of Japan," by Ernest Hart.

Geological, 8.

THURSDAY, 25th.—Royal, 4.30.

Institute of Electrical Engineers, 8.

Royal Institution, 3. "Some Recent Biological Discoveries," by Prof. E. Ray Lankester, M.A.

FRIDAY, 26th.—Royal Institution, 9. "On Optical Projection,"

by Sir David Salomons, M.A.

Physical, 5. "On Modes of Representing Electromotive Forces and Currents in Diagrams," by Prof.

S. P. Thompson, F.R.S. "On the Flexure of Long Pillars Under their Own Weight," by Prof.

M. FitzGerald, M.A. "On Choking Coils," by

Prof. J. Perry, F.R.S.

SATURDAY, 27th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

THE CHEMICAL NEWS.

VOL. LXV., No. 1683.

THE SPECIFIC HEAT OF ALUMINIUM.*

By J. W. RICHARDS, Lehigh University.

THE determinations of the specific heat of aluminium are but few in number, and yet vary widely.

As soon as Sainte-Claire Deville had obtained a button of aluminium in 1855, his friend Regnault importuned him for a specimen with which to determine its specific heat, and although Deville knew that the metal he had made was far from pure, yet he yielded to Regnault's request and furnished him with three small pieces, which analysed—

Silicon	2·87
Iron	2·40
Copper	6·38
Lead	traces
Aluminium	88·35

Regnault determined the mean specific heat of this metal between 25° and 97° to be 0·2056. He attempted to calculate approximately the specific heat of pure aluminium by allowing for the impurities present. In doing this he assumed the specific heat of silicon to be 0·1425, it not having been then determined, and his calculation gave him 0·2181 as the number for pure aluminium. Had he, however, used what we now know to be the specific heat of silicon, 0·21, he would have calculated 0·2200 as the specific heat of pure aluminium between 25° and 97°.

A year later Regnault obtained aluminium about 97 per cent pure. He obtained for this, between 14 and 97°, 0·2122. Allowing for the impurities present, he calculated 0·2143 as the probable number for pure aluminium.

It may be remarked in passing, as a curious fact, that Regnault treats these mean values as if they were invariable constants, independent of the range of temperature through which they were determined.

Following Regnault came Kopp, who in 1863 made determinations with ordinary Parisian aluminium. He obtained 0·2020 as the mean value between 20° and 52°. However, no analysis is given of the metal used, and from a consideration of the way in which Kopp experimented, and the degree of accuracy which was possible in his experiments, it is evident that his results are of very little value. For instance, four determinations gave him—

0·1970
0·2000
0·2070
0·2020,

from which he simply deduces 0·2020 as an average value.

In 1882, Professor Mallet made some absolutely pure aluminium for his researches on the atomic weight, and he determined its mean specific heat between 0° and 100°, by means of a Bunsen ice calorimeter, to be 0·2253. Since no impurity was present in the metal, this determination is free from one of the sources of error of the previous ones.

More recently, Naccari, the noted Italian physicist, states that he obtains for the true specific heat of aluminium at various temperatures the following values:—

18°	50°	100°	200°	300°
0·2135	0·2164	0·2211	0·2306	0·2401

It will be noticed that these values indicate that the

specific heat increases 0·0095 per 100°, and lead to the formulæ—

$$S = 0·2116 + 0·000095 t$$

$$Sm = 0·2116 + 0·0000475 (t_1 + t_2),$$

in which 0·2116 is the true specific heat at 0°. The mean between 0° and 100° would be 0·2164, comparing well with Regnault's results, but much lower than Mallet's. It is not stated what was the purity of the metal used by Naccari.

The question which the writer set out to solve presented itself to him in this way: Who is nearest the truth, Regnault and Naccari, or Mallet?

I obtained some aluminium made by the Hall process, which analysed—

Silicon	0·07
Iron	trace
Aluminium	99·93

Since the atomic weight of silicon is almost identical with that of aluminium, it was felt safe to neglect the influence of the 0·07 per cent present.

Three methods of procedure were used. First, a large weight of aluminium (100—200 grms.) was put into an empty calorimeter, whose water equivalent had been accurately determined by experiment, and allowed to stand several hours. When the temperature was nearly constant, a known weight of water at a higher temperature was run in, and the total loss of heat calculated from the observations. This method gave mean specific heats between about 16° and 22°. Secondly, the aluminium was suspended in steam and dropped into the water in a calorimeter. This gave values from 20° to 100°. Thirdly, two exactly similar calorimeters were used. The aluminium and a platinum ball weighing 52 grms. were placed on a platinum support and heated together either in an air-bath to 120°, or in a small furnace up to 400°, 500°, and 600°. The platinum ball was dropped into one calorimeter and the lump of aluminium into another. From the heat given out by the platinum its temperature was calculated, and assuming that the aluminium had been at the same temperature, I had the data for calculating its mean specific heat.

The third method gave the most concordant results. The first method was used for such a small range of temperature that the experimental errors were large. The second method was defective in default of suitable apparatus to secure the instant transfer of the metal from the steam into the calorimeter. The third method had the advantage, that since the platinum and aluminium were taken out of the furnace together and were dropped almost simultaneously into the calorimeters, it could fairly be assumed that they would cool about the same amount in the two or three seconds during which they were exposed to the air.

The writer has made two experiments by the first method, five by the second, and sixteen by the third. Selecting those experiments which were experimentally the nearest to perfect ones, and correlating the data by the method of least squares, the following formulæ were arrived at:—

$$Sm = 0·2220 + 0·00005 (t_1 + t_2)$$

$$S = 0·2220 + 0·0001 t,$$

in which 0·2220 is the true specific heat at 0° C.

From these formulæ the following values will be shown:—

Temperature.	True Specific Heat.	Range of Temperature.	Mean Specific Heat.
0°	0·2220	0°—100°	0·2270
20°	0·2240		
100°	0·2320		
		0°—625° (melting-point)	0·2533
625° (melting-point)	0·2845		

Total caloric capacity to the m.p. } 158·3

* Read at the Chemical Section of the Franklin Institute, December 15, 1891.

It is seen that the author's results confirm Mallet's determination, as far as the true specific heat is concerned, and agree closely with Naccari's observation of its rate of increase with the temperature.

Atomic heat,—

$$0.2270 \times 27.02 = 6.13,$$

using the mean specific heat between 0° and 100° , as is done with almost all other metals.

THE ESTIMATION OF IRON AND ALUMINUM IN THE PRESENCE OF PHOSPHORIC ACID.*

By W. H. KRUG.

(Concluded from p. 90).

Experiments on the Glaser Method.

In the first estimations made by this method I noticed, when the alcohol was evaporated, the formation of crystals of calcium sulphate, and therefore discarded it, as these crystals would contaminate the phosphate precipitate.

Experiments on Jones's Method.

This method separated the calcium perfectly. In boiling off the alcohol I noticed the formation of aldehyd, which was accompanied by a reduction of the iron. It is therefore necessary before adding the ammonia to boil for a few moments with a few drops of nitric acid. Jones claims that the calcium is separated quantitatively, and that the alcohol is diluted sufficiently by the water present to keep the bases in solution. While working with this method I noticed that the ignited calcium sulphate was invariably slightly rose-coloured. Upon investigation I found this to be due to small quantities of iron, which were precipitated by the alcohol. I then tried to remove this by continued washing of the freshly precipitated calcium sulphate, but even after using a litre of 85 per cent alcohol I still found the calcium sulphate contaminated with iron. Here then there is a grave source of error which is no doubt due to the large quantity of alcohol used, as I never observed any iron in the calcium sulphate obtained by Glaser's method. Through lack of time I did not determine the quantities of iron thus taken down; but they were considerable, and increased with the percentage present in the original substance.

I was here curious to investigate the action of potassium and ammonium salts on the precipitation of the calcium, and my work led me to some astonishing results.

Four solutions were made as follows:—

1. An unknown solution of calcium phosphate, the latter being brought into solution by means of a little hydrochloric acid.
2. A solution of potassium chloride containing 1.0 gm. in 100 c.c.
3. A solution of ferric chloride containing 0.22 gm. Fe_2O_3 in 10 c.c.
4. A solution of ammonium chloride containing 1.0 gm. in 100 c.c.

The calcium was precipitated according to Jones. It was first estimated in the calcium phosphate solution, 25 c.c. being used with 10 c.c. of the ferric chloride solution.

Two estimations gave calcium sulphate:—

$$0.2519 \text{ gm.} \\ 0.2519 \text{ ,,}$$

These agree exactly, but both were slightly rose-coloured. A mixture was then made of 25 c.c. of calcium solution, 10 c.c. of the iron solution, and 5 c.c. of the

potassium chloride solution. Two estimations gave calcium sulphate:—

$$0.2785 \text{ gm.} \\ 0.2784 \text{ ,,}$$

Both of these were highly coloured with iron, and a qualitative examination revealed the presence of potassium.

Then 25 c.c. of the calcium solution, 10 c.c. of the iron solution, and 10 c.c. of the potassium chloride solution were mixed, and the calcium separated and weighed.

Two estimations gave calcium sulphate:—

$$0.2805 \text{ gm.} \\ 0.2800 \text{ ,,}$$

These two contained still more iron, and potassium was again present.

The influence of the ammonium chloride was then tried. I again used 25 c.c. of the calcium solution, 10 c.c. of the iron solution, and 5 c.c. of the ammonium chloride solution.

Two estimations gave calcium sulphate:—

$$0.2541 \text{ gm.} \\ 0.2543 \text{ ,,}$$

and on using the same mixture with 10 c.c. of the ammonium chloride solution, I obtained calcium sulphate:—

$$0.2563 \text{ gm.}$$

It thus appears that the presence of potash and ammonium salts increases the amount of iron present in the calcium sulphate. The presence of the alkali shows that the alcohol precipitates it and the iron as double sulphates or alums which are much less soluble in alcohol than any other ferric and aluminic salts.

Ammonium salts do not exercise this influence to so great an extent as potassium salts, but still sufficiently to vitiate the subsequent results. This renders the Jones method inapplicable in cases where these alkalies are present, as in soils and ashes, and the presence of small quantities of iron, even in those instances where no alkali was added, indicates that the quantity of alcohol prescribed by Jones is too high.

It is of interest to note the manner in which the presence of potassium or ammonium salts influenced the form in which calcium sulphate precipitated. Usually when the alcohol is added the precipitate in a very short time becomes crystalline. When these salts, however, are present, it precipitates in a flocculent form, and remains so, even if allowed to stand over night.

Finding in this manner possibilities of error which rendered both methods doubtful, I decided to try the Stutzer method as modified by Vogel, with previous removal of the calcium, according to Glaser's directions. In two other portions of the solution the calcium was precipitated according to Jones.

I append the results obtained with a phosphate rock:—

Sample.	Method.	Weight material. Gm.	Weight precipitate.	Per cent combined oxide.
I ..	Glaser-Stutzer.	0.500	0.0085	1.70
I ..	"	0.500	0.0084	1.68
I ..	Jones-Stutzer.	0.500	0.0028	0.56
I ..	"	0.500	0.0032	0.64

We see that much less iron and aluminum was present in the alcoholic filtrate obtained by Jones's method, and this is another proof that some of it is retained by the calcium sulphate.

I now turned to the molybdate method used by Mr. McElroy, it appearing that this should, if properly and carefully carried out, give accurate results. On a preceding page I have given a description of this method. It is necessary to resort to a double precipitation of the hydrates, as when the ammonia is first added a small amount of molybdic anhydride is liable to separate out in the form of a white powder. If the liquid is kept as cool

* Read before the Washington Chemical Society, Nov. 12, 1891. From the *Journal of Analytical and Applied Chemistry*, Vol. v., No. 12.

as possible and the ammonia added only in slight excess, this is reduced to a minimum. It never occurs in the second precipitation.

The method was tried on four phosphate rocks and gave the following results:—

Sample.	Weight material.	Weight precipitates.	Per cent oxides.
1	0.200 grm.	0.0052	2.60
1	0.200 "	0.0053	2.65
2	0.200 "	0.0022	1.10
2	0.200 "	0.0021	1.05
3	0.200 "	0.0064	3.20
3	0.200 "	0.0068	3.40
4	0.200 "	0.0099	4.95
4	0.200 "	0.0100	5.00

Sample 1 is the same as that to which the Stutzer method was applied, and we see that the molybdate method gives much higher results, which from the nature of the method are undoubtedly much more accurate.

This method was tried with success in the analysis of soils by Mr. J. L. Fuelling. By permission I include some of his results.

Sample.	Per cent oxides.	Sample.	Per cent oxides.
a	2.32	c	1.19
a	2.26	c	1.19
b	1.48	d	1.23
b	1.55	d	1.23

The greatest deviation between duplicates, we see, is 0.07 per cent, an allowable difference which occurs in all analytical work.

All in all, the above shows that this method is to be preferred to all others, being as short and as rapid as the alcohol method, giving more accurate and concordant results, and giving the oxides in a form which is easily rendered soluble, so that the iron can be accurately estimated.

REPORT ON DETERMINATION OF NITROGEN.*

By E. B. VOORHEES.

As your reporter on nitrogen, I now have the honour to present the results of the work done by the Association this year. As far as your reporter has been able to review the foreign and American journals, he has not found that the past year has developed any particularly new or desirable additions to our present official methods. The Report, therefore, will include chiefly (1) the results secured by members of the Association, and (2) recommendations and suggestions.

Early in the year a circular letter asking co-operation in the work of the Association was sent to all chemists connected with experiment stations, to seven commercial chemists, and to such others as were so entitled by our constitution, numbering in all about forty. Thirty-two, representing twenty-six stations, the United States Department of Agriculture, and that of Virginia, and five commercial chemists, signified their desire to take part in the work. Three samples were sent to each of these early in March, accompanied by another circular letter, asking that a moisture determination be made in each of the samples, and that the nitrogen determination be made according to the official and alternate methods. The Report for 1889 had not then been distributed, hence they were asked to use those methods described in the Report of the Association for 1888, with such additional modifications as were recommended by the reporter in 1889. The samples were marked 1, 2, and 3, and were made up as follows:—

Description of samples.	Per cent nitrogen.	Grms.
No. 1.—Potassium nitrate containing	13.72	400
Sodium nitrate containing	16.14	56
Calculated per cent of nitrogen	14.01	
No. 2.—Linseed meal containing	7.15	250
Cotton-seed meal containing	5.50	250
Sodium nitrate containing	16.14	100
Calculated per cent of nitrogen	7.96	
No. 3.—Dried blood containing	13.92	300
Ammonite containing	13.02	300
Calculated per cent of nitrogen	13.47	

The Report includes the work of twenty-four chemists, representing but fourteen of the twenty-five experiment stations which early in the season desired to co-operate, and the departments of agriculture of the United States and of Virginia. No commercial chemists are represented.

Results.

The percentage of moisture was not reported by all of the chemists, and since the amounts reported in samples 1 and 3 were very uniform, all results are based upon original substance. The method of standardising the acid was mentioned in only three reports; in these the tetraoxalate was used with good results.

Kjeldahl Modified for Nitrates.

Analysts.	Per cent nitrogen.	
	No. 1.	No. 2.
Walker Bowman (Virginia Experiment Station)	13.95	7.49
R. C. Kedzie (Michigan Experiment Station)	14.04	8.40
H. R. Baldwin (West Virginia Experiment Station)	13.73	7.88
F. B. Carpenter (North Carolina Experiment Station)	13.76	7.36
H. J. Patterson (Maryland Experiment Station)	13.82	7.66
B. F. Finney (Virginia Experiment Station)	13.86	7.77
R. H. Gaines (Virginia Department of Agriculture)	14.13	7.68
T. C. Trescot (United States Department of Agriculture)	13.40	7.65
J. M. Bartlett (Maine Experiment Station)	14.12	7.64
L. H. Merrill (Maine Experiment Station)	14.20	7.74
W. H. Beal (Massachusetts Experiment Station)	13.80	7.61
F. W. Morse (New Hampshire Experiment Station)	14.13	8.04
C. L. Parsons (New Hampshire Experiment Station)	14.05	7.79
C. D. Woods (Stoors Experiment Station)	14.04	7.97
Duncan Adriance (Texas Experiment Station)	13.79	
A. L. Winton and R. S. Curtis (Connecticut Experiment Station)	13.74	7.74
L. A. Voorhees and C. S. Cathcart (New Jersey Experiment Station)	14.04	7.94
B. B. Ross (Louisiana Experiment Station)	14.11	7.87
G. L. Holter (Pennsylvania Experiment Station)	13.45	7.81
M. A. Scovell (Kentucky Experiment Station)	14.08	7.99
A. M. Peter (Kentucky Experiment Station)	14.02	8.03
H. E. Curtis (Kentucky Experiment Station)	13.99	7.93
Average of whole number	13.91	7.80
„ twenty	13.96	7.81

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

Kjeldahl Method.

Analysts.	Per cent nitrogen. No. 3.	Per cent nitrogen.			
		No. 1.	No. 2.	No. 3.	
Walker Bowman (Virginia Experiment Station)	13'35				
R. C. Kedzie (Michigan Agricultural College Experiment Station) ..	13'72				
H. R. Baldwin (West Virginia Experiment Station) ..	13'45				
F. B. Carpenter (North Carolina Experiment Station) ..	13'40				
H. J. Patterson (Maryland Experiment Station)	13'55				
B. F. Finney (Virginia Experiment Station) ..	13'72				
R. H. Gaines (Virginia Department of Agriculture) ..	13'77				
T. C. Trescot (United States Department of Agriculture) ..	13'16				
J. M. Bartlett (Maine Experiment Station) ..	13'54				
L. H. Merrill (Maine Experiment Station) ..	13'63				
W. H. Beal (Massachusetts Experiment Station)	13'26				
F. W. Morse (New Hampshire Experiment Station) ..	13'31				
C. L. Parsons (New Hampshire Experiment Station) ..	13'46				
C. D. Woods (Stoors Experiment Station) ..	13'49				
Duncan Adriance (Texas Experiment Station) ..	13'07				
A. L. Winton and R. S. Curtis (Connecticut Experiment Station) ..	13'43				
L. A. Voorhees and C. S. Cathcart (New Jersey Experiment Station) ..	13'46				
B. B. Ross (Louisiana Experiment Station) ..	13'71				
G. L. Holter (Pennsylvania Experiment Station)	13'08				
M. A. Scovell (Kentucky Experiment Station) ..	13'63				
A. M. Peter (Kentucky Experiment Station) ..	13'53				
H. E. Curtis (Kentucky Experiment Station) ..	13'49				
Average ..	13'46				

Ruffle Method.

Analysts.	Per cent nitrogen.		
	No. 1.	No. 2.	No. 3.
F. B. Carpenter (North Carolina Experiment Station) ..	13'49	7'41	13'39
H. J. Patterson (Maryland Experiment Station) ..	13'72	7'70	13'71
T. C. Trescot (United States Department of Agriculture) ..	13'82	7'75	13'55
W. H. Beal (Massachusetts Experiment Station) ..	13'84	7'62	13'28
G. L. Holter (Pennsylvania Experiment Station) ..	13'30	7'80	—
Average ..	13'63	7'66	13'48

Soda-Lime Method.

Analysts.	Per cent nitrogen.	
	No. 1.	No. 2.
H. J. Patterson (Maryland Experiment Station)	13'73	
H. E. L. Horton (United States Department of Agriculture) ..	13'46	
W. H. Beal (Massachusetts Experiment Station)	13'29	
C. D. Woods (Stoors Experiment Station) ..	13'56	
New Jersey Experiment Station ..	13'44	
G. L. Holter (Pennsylvania Experiment Station)	13'30	
Average ..	13'46	

Absolute Method.

Analysts.	Per cent nitrogen.	
	No. 1.	No. 2.
T. C. Trescot (United States Department of Agriculture) ..	13'77	7'79
A. L. Winton and R. S. Curtis (Connecticut Experiment Station) ..	—	7'67

Table of Averages.

Method.	No. of sample.	No. of analysts.	Per cent nitrogen.			
			Average.	Highest.	Lowest.	Diff.
Kjeldahl ..	3	22	13'46	13'77	13'07	0'70
„ modified	1	22	13'91	14'20	13'40	0'80
for nitrates	2	21	7'81	8'40	7'36	1'04
Ruffle ..	1	5	13'63	13'84	13'30	0'54
	2	5	7'66	7'80	7'41	0'39
	3	4	13'48	13'71	13'28	0'43
Soda-lime ..	3	6	13'46	13'73	13'29	0'44

All of the chemists represented reported results by the official methods; those reported by the alternate are in addition to the official.

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 30TH, 1892.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, February 6th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, 179 were found to be clear, bright, and efficiently filtered, three being recorded as "very slightly turbid" (V.S.T.).

Except for the occurrence of these three instances of but "very slight turbidity," the condition of the water supply to the metropolis during the month of January was entirely satisfactory. Thus, taking the Thames-derived supply for comparison, the mean degree of colour-intt was found to be 12'4:20, as against 18'7:20; the mean amount of oxygen expended in oxidation to be 0'052 grain, as against 0'079 grain; and the mean amount of organic carbon to be 0'158 part in 100,000 parts, as against 0'240 part in the previous month's supply. Moreover, the maximum amount of organic carbon in any single sample examined was found to be reduced from 0'319 part in December to 0'204 part in January, the next highest amount recorded during the month being only 0'189 part in 100,000 parts of the water.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE USE OF ASBESTOS IN FILTRATION.

By W. P. BARBA.

IN the usual manner of determining manganese by Ford's admirable method, a great deal of time is used up in avoiding the difficulties introduced by the silica present in the steel or iron. The solution of the drillings in HCl, the expulsion of the HCl by HNO₃, and the tedious filtration on the pump, may all be avoided by the use of finely divided asbestos in HNO₃, as pointed out by me in the filtration of carbon sponge (*Journal of Analytical and Applied Chemistry*, vol. v., 596).

The asbestos is best prepared by triturating in a porcelain mortar to moderate fineness, washing with HNO₃, and may be kept suspended in strong HNO₃ for use. The method as now practised at Midvale may readily be carried through in forty minutes, and is as follows:—

5 grms. of steel are dissolved in 80 c.c. HNO₃, specific gravity 1·20, and boiled to one-half that bulk. 75 c.c. of strong HNO₃ are then added, and boiled for about five minutes more. The usual portion of KClO₃ is added—about 5 grms.—and the solution boiled till precipitation is effected. The beaker is then withdrawn from the plate and a quantity of finely divided asbestos in HNO₃ is added. The solution, when sufficiently cooled, is filtered on a tight asbestos plug, washed twice with HNO₃, and then with water till all acid is removed. The plug with the precipitate is blown back into the same beaker, ferrous sulphate added, and the titration carried out as usual.

It will be found that filtration is very much facilitated by the presence of the fine asbestos, and that the solution of the precipitate in the FeSO₄ is almost instantaneous, thus removing the difficulties of the two most tedious operations of the method.—*Journal of Analytical and Applied Chemistry*, vi., No. 1.

ON THE MOST HIGHLY OXIDISED COMPOUND OF SULPHUR.

By MORITZ TRAUBE.

BERTHELOT (*Comptes Rendus*, cxii., p. 1481) and Hugh Marshal (*Proc. Chem. Soc.*, 1891, p. 771) have demonstrated the true existence of a persulphuric acid, H₂S₂O₈. Both these chemists considered themselves thereby entitled in denying the existence of the compound SO₄ (*Berichte*, xxix., 1764) which I had demonstrated, though without any re-examination of my experiments. In consequence, I considered a repetition of my experiments necessary, which has been kindly undertaken by W. Traube. The former results have been completely confirmed.

The solution of the substance in question in phosphoric acid was obtained as before, by treating the electrolytic 70 per cent sulphuric acid with excess of barium phosphate. Its active oxygen, i.e., that which oxidises ferrous sulphate, was titrated with a solution of this salt. The precipitate of barium sulphate, obtained by boiling the phosphoric solution with hydrochloric acid and barium chloride, was extracted in some cases with dilute boiling hydrochloric acid in order to remove any barium phosphate which had been carried down; in other cases it was first treated in the cold with a dilute solution of soda, and then afterwards with hydrochloric acid.

Hydrogen peroxide was not present if the electrolysed acid was used for analysis whilst recent, or, if it was formed in small quantities, after standing for several days it was destroyed as previously, before the determination of the active oxygen by the quantity of permanganate required.

The analysis of three different phosphoric solutions gave the respective mean quantities of 15·0 m.grms., 18·1 m.grms., and 15·7 m.grms. of active oxygen. The

proportion of O to SO₃ was 1:5·1. Six parts by weight of the sulphur compound, 5 parts by weight SO₃, 1 part by weight of oxygen being eliminated.

Hence, there doubtless exists in the electrolysed sulphuric acid not persulphuric acid but SO₄; for we cannot assume that so indifferent a substance as barium phosphate can split up persulphuric acid into SO₄ and H₂SO₄. On the other hand, it is quite intelligible that on saturating the electrolysed sulphuric acid with strong bases, SO₄ and H₂SO₄ may combine under their influence to persulphuric acid.

In my former investigation I was led by my experiments on electrolysed sulphuric acid saturated with strong bases to the conclusion that SO₄ is indifferent. I had, of course, taken as my point of departure the assumption (seemingly a matter of course), that the solution, when neutralised, contains SO₄. But, as already mentioned, on saturating electrolysed sulphuric acid with an alkali, there is formed a persulphate. The question of the indifference of SO₄ must therefore be decided by further researches. Preliminary experiments with the phosphoric solution of the compound in question seem to confirm its indifferent character.

On the basis of experiments I have placed SO₄—which must now be considered as persulphuric acid—along with the holoxydes, the compounds of the type of hydrogen peroxide, because in the first place it very readily forms hydrogen peroxide; secondly, like this, it evolves oxygen with the peroxides of lead, manganese, and silver, in presence of acids, and, thirdly, that it is decomposed in contact with platinum and acids, with liberation of oxygen.

On the contrary, Berthelot and Marshal ascribe to persulphuric acid the same constitution as to permanganic and perchloric, although the latter do not evince the characteristic reactions of the holoxydes, and permanganic acid even destroys hydrogen peroxide energetically. Marshal himself has observed that potassium persulphate is not isomorphous with potassium perchlorate.—*Ber. Deutsch. Chem. Gesell.*

THE DIRECT COMBINATION OF CHLORINE WITH METALS.

By U. KREUSLER.

A MEMOIR by Gautier and Chaubry (*Comptes Rendus*, vol. cxiii., pp. 597—600), on "The Direct Combination of Chlorine with Metals," recalled to the mind of the author an observation made some time ago. Among the instances given in the text-books for demonstrating combustion in chlorine gas, there figures a spiral of thin brass wire, to which was attached a tuft of spurious leaf-gold to facilitate ignition.

The text generally speaks simply of chlorine, but sometimes of dry chlorine gas. The drying process is mostly dispensed with, and the experiment, as it is well known, succeeds very easily. But when the author once by accident used the dried gas, it failed unexpectedly, and the metallic surfaces remained perfectly bright. The remembrance of certain kindred phenomena, recently observed in case of oxygen, showed an escape from the difficulty. It was sufficient to allow a drop of water to fall anywhere into the vessel or to insert a moistened glass rod in order to induce immediate and energetic combustion.

It may be mentioned that the gas in question had not been dried with especial care. It had been simply passed through a washing-bottle filled with sulphuric acid and collected by displacement in dry bottles. Powdered antimony caught fire at once in the gas, either because the co-operation of water is not needed in this case, or because sufficient moisture adhered to the material.—*Ber. Deut. Chem. Gesell.*, vol. xxiv., p. 3947.

ON THE
STABILITY OF SILVER SULPHITE.

By W. H. SODEAU.

ACCORDING to Berthier (*Ann. Chem. et Phys.*, vol. iii., 7, 82), silver sulphite is decomposed when boiled with water or heated to 100° C. in air. The blackening of the silver precipitate on boiling is sometimes given as a confirmatory test for sulphites. According to Muspratt, silver sulphite becomes dark purple and ultimately black on exposure to air, but according to Fourcroy the crystals are unaltered even in sunlight. (Quoted in Watts's "Dictionary," old edition).

To prepare the substance used in this investigation, re-crystallised AgNO_3 was dissolved in water, and SO_2 passed into the solution; the precipitate (consisting of anhydrous needles, $\frac{7}{80}$ th inch and less in length) was well washed by decantation with warm distilled water, and dried in a vacuum over H_2SO_4 , saturated with chromic acid, taking special precautions to avoid reductions by the volatile compounds in the vaseline used to render the apparatus air-tight. Several specimens were thus prepared and divided into small portions, which were introduced into tubes, some dry, and others with water, and sealed. The tubes were then heated or exposed to light, with the results given in the table. The mixtures mentioned are intended to roughly indicate the amount of darkening, but are not intended to represent the actual colour.

Condition.	Treatment.	Result (parts by weight).
Dry.	100° C. for 1 hour	Slightly affected, whiter than ordinary white paper.
"	130° C. for 1 hour	About as dark as 1 part graphite, 8 parts CaCO_3 .
"	200° C. for $\frac{1}{2}$ hour	About as dark as 1 part graphite, 2 parts CaCO_3 .
"	{ Placed substance on porcelain at about 400° C.	Became black in a few seconds.
In water.	100° C. for 1 hour	About as dark as 1 part graphite, 25 parts CaCO_3 .
Dry.	{ Daylight at south window for two weeks.	About as dark as 1 part graphite, 50 parts CaCO_3 .
In water.	" "	About as dark as 1 part graphite, 30 parts CaCO_3 .

Some silver sulphite which had been exposed to dry air for four weeks was found to contain only a minute trace of sulphate. A portion was kept under water and exposed to air; a small quantity of sulphate was detected after two weeks.

Chemical Laboratory,
King's College, London, W.C.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 12th, 1892.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

THE Report of the Council was read by the PRESIDENT, as was also the obituary notices of Prof. W. Weber, late Honorary Member, Mr. W. G. Gregory, and Prof. James Couch Adams. A list of additions to the Library accompanied the Report.

Dr. E. ATKINSON read the Treasurer's Statement, showing a gain of about £240.

On the motion of the President the Reports of the Council and of the Treasurer were unanimously adopted. Prof. Van der Waals was elected an Honorary Member of the Society.

Prof. REINOLD proposed a cordial vote of thanks to the Lords of the Committee of Council on Education for the use of the rooms and apparatus in the Royal College of Science. This was seconded by Prof. S. P. THOMPSON and carried unanimously. A similar note was accorded to the auditors, Dr. Fison and Mr. H. M. Elder, on the motion of Mr. W. BAILY, seconded by Dr. C. V. BURTON.

The following gentlemen were declared duly elected to form the New Council:—

President—Prof. G. F. Fitzgerald, M.A., F.R.S.

Vice-Presidents—Prof. A. W. Rücker, M.A., F.R.S., Walter Baily, M.A., Prof. O. J. Lodge, D.Sc., F.R.S., Prof. S. P. Thompson, D.Sc., F.R.S.

Secretaries—Prof. J. Perry, D.Sc., F.R.S., 31, Brunswick Square, W.C., and T. H. Blakesley, M.A., M.I.C.E., Royal Naval College, Greenwich.

Treasurer—Dr. E. Atkinson, Portesbery Hill, Camberley, Surrey.

Demonstrator—C. Vernon Boys, F.R.S., Physical Laboratory, South Kensington.

Other Members of the Council—Shelford Bidwell, M.A., LL.B., F.R.S., W. E. Sumpner, D.Sc., Major-General E. R. Festing, R.E., F.R.S., J. Swinburne, Prof. J. V. Jones, M.A., Rev. F. J. Smith, M.A., Prof. W. Stroud, D.Sc., L. Fletcher, M.A., F.R.S., G. M. Whipple, D.Sc., James Wimshurst.

A vote of thanks to the officers of the Society was proposed by Mr. SWINBURNE, seconded by Mr. A. P. TROTTER, and carried unanimously.

The CHAIRMAN then invited suggestions towards improving the working of the Society.

In response, Prof. S. P. THOMPSON said that as the Society has been established fifteen or sixteen years, and had amply justified its existence, the time had now arrived for giving fuller recognition to the privileges of members. He thought they had earned the right to be called "Fellows," and that this ought to be signified by some distinctive title.

Mr. J. SWINBURNE suggested that before papers were brought before the meetings they should be read by a Member of the Council. If suitable, they should then be printed and proofs sent to members who applied for them. Mathematical papers could then be taken as read; and the discussions would be more interesting and to the point. It would also be an advantage if communications on kindred subjects could be taken the same day and discussed together. Papers on purely technical subjects should go to the Technical Societies.

Prof. AYRTON, in reply to Mr. Swinburne, said the members had the matter of papers in their own hand, for, as pointed out in the Report of the Council, if they would only send in the papers early enough, the secretaries would be glad to group them in the way suggested.

Referring to Prof. THOMPSON's remarks, he said he had often thought it would be an advantage to have another class of members in the shape of "students," who should hold meetings amongst themselves.

Mr. A. P. TROTTER said the Society was unique in many respects, and thought it was not desirable to have different grades of membership.

Dr. C. V. BURTON agreed with Mr. Trotter, and said that, even if Prof. Thompson's suggestion was adopted, means should be provided that persons could be admitted into the Society without claiming any distinction therefrom.

Prof. S. P. THOMPSON, referring to the communications brought before the Society, said it was not necessary that all should possess great novelty. Descriptions of new arrangements of apparatus, of diagrams, and exhibits of modern instruments were of great interest to members.

The CHAIRMAN pointed out that at the early meetings of the Society exhibitions of instruments were frequent, and said the Council would be glad if instrument makers would send apparatus to be shown at any of the meetings.

The meeting was resolved into an Ordinary (Science) Meeting, and Messrs. W. R. Bower and E. Edsen were elected Members.

Prof. S. P. THOMPSON communicated a "Note on Supplementary Colours," and showed experiments on the subject.

As white light can be divided into pairs of "complementary colours," so any coloured light, not monochromatic, can be split up into pairs of tints; these the author, for want of a better name, has called "supplementary colours." For producing such colours, two methods were used.

In the first one, a spectrum of coloured light was formed by a direct-vision spectroscopic and re-combined on a screen. By interposing a narrow prism between the spectroscopic and screen, a portion of the spectrum was separated from the rest, and various pairs of supplementary colours thereby obtained.

In the other method, polarised light, a quartz plate, and a double-image prism were used to form two patches of complementary colours. On interposing a coloured medium, the patches became supplementary and varied in tint as the prism was rotated. The chief peculiarity of supplementary colours was the great variety of tints that could be obtained from a single medium; permanganate of potash in dilute solutions being particularly rich in this respect. The author had also noticed that the eye was not very sensitive to orange coloured rays. When experimenting by the second method he had observed that with any composite light one of the supplementary patches could be got of a greyish hue, and the other nearly a pure spectrum tint. He thus unexpectedly verified Abney's law that any colour could be produced by diluting some spectrum tint with white light.

Capt. ABNEY said that it was very interesting to see the grey colour and the supplementary colours shown by the author. Genl. Festing and himself had experimented on colour phenomena by methods quite different from those used by Prof. Thompson, for they had matched colours by adding white light to pure spectrum tints until a match was produced. Greater purity of colour could be obtained in this way.

A paper "On Modes of Representing Electromotive Forces and Currents in Diagrams," by Prof. S. P. THOMPSON, F.R.S., was postponed.

NOTICES OF BOOKS.

Cooley's Cyclopædia of Practical Receipts and Collateral Information in the Arts, Manufactures, Professions, and Trades; including Medicine, Pharmacy, Hygiene, and Domestic Economy. Designed as a comprehensive Supplement to the "Pharmacopœia, and General Book of Reference" for the Manufacturer, Tradesman, Amateur, and Heads of Families. Seventh Edition. Revised and greatly Enlarged by W. NORTH, M.A., F.C.S. London: J. and A. Churchill. Large 8vo., 2 vols., pp. 1827.

This valuable and generally admired work is now much more than a mere collection of recipes, however complete. Subjects not merely medical, pharmaceutical, or chemical, are made the subject of able articles in its pages.

Thus, in turning the volumes over, we find notices of anachronism, anagram, anastatic printing, arabesques, arcuæd, aurora, bells, and telephones. In short, the work has a general encyclopedic character, and we are

sometimes perplexed to see why the lines have been drawn precisely as we find them. If, e.g., bells are to be included why not cymbals and drums? If telephones are noticed why not telegraphs? We must not be understood as denying the fact that a great part of the book is devoted to such classes of subjects as balsams, plasters, pills, powders, oils, ointments, solutions, &c. Secret medicines and modes of treatment are also dealt with more in the interest of the public than of the advertising fraternity. But we see no mention of electropathy, the ammoniophone, the faith-cure, or not a few of the other fashions of the day.

There are a number of able articles on different subjects connected with sanitary science, though the dissertation on sewage treatment might be, in our opinion, improved by a judicious revision. But the statements of the Rivers' Pollution Commission are still reproduced without the grain of salt. We find a statement by an author whom we shall not advertise, to the effect that: "There is no chemical process that cannot be worked to greater advantage during two months of the year than during twelve, or applied to a small quantity of sewage at a less cost than to a large." It is difficult to imagine by what process this paradoxical conclusion can have been reached. It is a general rule that so long as a raw material can be always obtained, it is more profitable to work all the year round than for a short time, and also on a large than on a small scale. All industrialists are aware of the impolicy of allowing plant and machinery to stand idle.

The series of articles on the diseases of crops occasioned by insects, parasitic microphytes, &c., are excellent,—those, at least, which bear the signature of Mr. Whitehead. Some unsigned passages on similar subjects are drawn up on ultra-Watertonian principles, and would seem by implication to discountenance the destruction of locusts, &c.

We find a few legal articles bearing on sanitary questions, such as common lodging-houses, notification, nuisances, infectious diseases, &c., and which will be serviceable as calling the attention of householders to their responsibilities.

The adulteration of food and drugs has also not been ignored, though the author wisely does not attempt to instruct the lay reader in the detection of this class of frauds.

The articles on dyes and colours are, perhaps, the least satisfactory part of the work, such important classes of tinctorial agents as the azo-dyes having been omitted.

We cannot do otherwise than pronounce the work on the whole most satisfactory. If we may venture on a suggestion we should recommend that in the certain case of a new edition the writers should take their point of view not from the United Kingdom, but from the British Empire. This extended aim would, of course, necessitate the revision of the sections on sanitary topics, on diseases, and on the pests affecting crops.

Systematic Mineralogy, based on a Natural Classification. With a General Introduction. By THOMAS STERRY HUNT, M.D., LL.D. New York: Scientific Publishing Co.

OF all the sciences which treat of visible, tangible objects and their mutual relations, mineralogy is, at any rate in Britain, the least popular. It is also the one which has been least fecundated by the grand principle of evolution. Whether these two facts, both, in our opinion, worthy of regret, are causally connected, we do not venture to decide. We may, however, venture to hope that the appearance of Dr. Hunt's elaborate work will attract more public attention to a science which combines in no small degree intrinsic interest and practical importance. It will be known to our readers that among systematic authors on mineralogy there have appeared two conflicting systems. We have the natural-history method, —a cumbrous word,—and the chemical method, the

former advocated by Mohs, Dana, and Breithaupt, and the latter supported by Berzelius and Rammelsberg.

Our author aims at a reconciliation of these two seemingly conflicting principles. He argues, with full justice, that "chemical and physical characters are really dependent on each other, and present two aspects of the same problem which can never be solved but by the consideration of both."

In his first chapter Dr. Hunt ventures on a step of doubtful expedience, a re-classification of the sciences, which he arranges as physiography and physiology. He is perfectly correct in stating that "the words physiologist and naturalist were formerly synonymous in the English language." But the term physiology has by common consent been restricted to the functional activity of plants and animals, and any return to the old usage will merely promote confusion. He places morphology under the head of bio-physiology, whilst its true position is surely along with taxonomy (botany and zoology), under the descriptive or, better, the statical phase of organic science.

We must here remark that on the Continent biology is made nearly synonymous with physiology, whilst with us it is the sum total of organic science, and divided into a statical phase (morphology and taxonomy), and a dynamical phase (embryology and physiology).

The author in setting forth the chemical basis of his system, proposes four classes, metallacæ, halidacæ, oxydacæ, and pyricautacæ. The first of these classes embraces the metals, their alloys and their compounds with sulphur, selenium, tellurium, phosphorus, arsenic, antimony, and bismuth. This first, or metallic class, is subdivided into two groups, metallometallata and spathometallata.

The halidacæ consist of four orders, the fluorinea, the chlorinea, the brominea, and the iodinea. The oxydacæ include the oxides, borates, carbonates, aluminates, silicates, aluminosilicates, phosphates, arsenates, sulphates, &c. Dr. Hunt's last class, the pyricautacæ, is divided into carbata, forms of carbon, and hydrocarbata, petroleum, resins, asphalts, and coals. For the details of this system we must refer our readers to the work itself, remarking that the principles of descriptive and determinative mineralogy are not here brought forward.

We cannot discover the author's position with regard to the principle of evolution. He, however, pronounces Mr. Ridsdale's hypothesis of the "survival of the most inert," to be "but another statement of the formula of the survival of the fittest." Precisely so, but it is a statement applicable to the conditions of objects which have no vital cycle and no successions of generations, seeing that nothing further has been heard of Brame's "utricular condition." The student of mineral chemistry cannot, we think, be indifferent to Dr. Hunt's work.

Scientific Correspondence of Joseph Priestley. Ninety-seven

Letters addressed to Joseph Wedgwood, Sir Jos. Banks, Captain James Keir, Jas. Watt, Dr. W. Withering, Dr. Benjamin Rush, and others. Together with an Appendix.—I. The Likenesses of Priestley, in Oil, Ink, Marble, and Metal. II. The Lunar Society of Birmingham. III. Inventory of Priestley's Laboratory in 1791. Edited, with copious Biographical, Bibliographical, and Explanatory Notes, by HENRY CARRINGTON BOLTON. New York: Privately Printed.

DR. CARRINGTON BOLTON has already made a very valuable contribution to the early history of chemistry in the shape of a work showing the light which alchemy receives from a study of numismatics. He now confers an additional benefit upon the chemical world by a work which brings into fuller relief the opinions and character of one of the most remarkable—and, we might say, epoch-making—men of the last century. Every chemist knows that, in addition to his important researches on gases, Priestley was the "first and true" discoverer of oxygen, and that he still adhered to the phlogiston system which he had

thus undermined. But from this volume we learn for the first time that to the end of his days phlogiston was his "dominant idea," and that he continued to hope for the refutation of the Lavoisierian system and of the restoration of phlogiston to its old prominence.

Another of the unfortunate phases of his character is also noticed. It is well known that his attention was not solely confined to chemistry, or, indeed, to science in general. Much of his time was frittered away on theological and political discussion. His friend Edward Gibbon had recommended him to keep to science and leave miracles alone, reminding him that if Servetus is now remembered, it is not on account of his denial of the doctrine of the Trinity, but because he was one of the forerunners of William Harvey. This good advice, however, was thrown away. We read here that: "Believing as he did that his reputation would be founded on his theological system, Priestley, in his Memoirs, has but little to say of his work in science; and Mr. Rutt, evidently sharing this view, adds nothing whatever which can extend or illustrate Priestley's reputation as a chemical philosopher." *Hinc illæ lachrymæ!* Priestley was not a martyr of science; he was persecuted not as a *savant*, but as a religious and political heretic, whose chemical discoveries, in those critical times, were not considered sufficient to outweigh his other shortcomings.

It can scarcely be denied that by taking the part he did, he to some extent brought science into contempt alike with the ruling powers and with the mob. It appears that during the Birmingham riots the cry was raised "No philosophers," and that some persons to escape the fury of the rioters wrote "No Philosophers" on the front of their houses. The "Lunar Society"—an unhappily named scientific society, at Birmingham—seems never to have recovered from the shock of the riots. The old members died, and no successors were elected in their room. We have never been able to suppress our regret that Priestley had not given his undivided attention to chemistry, and the perusal of these letters by no means alters our view. In such a fraction of his time he effected so much, he would surely have done more could he have kept out of the bitter waters of controversy. It may, however, still be contended that the versatility and restless activity of his disposition would not have allowed him to devote his life to one subject.

We find here an acknowledgment on the part of Priestley that he was more happy in observing phenomena than in their interpretation; a statement which his career fully bears out. As an observer he was wonderful.

We note (p. 206) an utterance against which we must protest. Says Dr. Carrington Bolton: "The French theory of combustion was but slowly accepted by the conservative Englishman." In our day, France is the country in which new scientific theories meet with the tardiest acceptance!

Dr. Carrington Bolton's work reminds us strongly of the parallelism between Priestley and Lavoisier; both great chemists, rivals for the capital discovery of their time, and persistent opponents in theory; both involved in the tempest which enwraps the close of the eighteenth century; the one done to death by the Revolution to the cry "the Republic has no need of chemists;" the other hunted about by the opponents of the revolution to the equally brutish cry "No Philosophers."

We have here a subject for a modern Plutarch. Should such an one spring up, he will find the collection of letters before us a valuable material for his task.

Dr. Bolton's work can only be obtained from Mr. Edmund F. Brown, 180, Warren Street, Brooklyn, N.Y., the price being \$2½ per copy.

Researches on Sodium Isopropylate.—M. de Forcrand.—Sodium isopropylate is a perfectly white powder, which can be preserved only in bottles hermetically sealed and filled with hydrogen or nitrogen. Its composition is $C_6H_7NaO_2$.—*Comptes Rendus*, cxiv., No. 6.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I should like to be allowed space for a short reply to the letters in your last issue commenting on mine on p. 84.

Mr. Allen's is open and honest, but, fortunately or unfortunately, he is gifted with a vivid imagination, and consequently many of the assertions contained in his letter would in any one else be characterised as reckless: they have no tangible basis. One or two by way of sample.

No. 1.—In reference to the omission of the words "consulting and"—which, by the way, Mr. Allen quotes "and consulting"—he accuses me of suggesting "that the omission was designed." What I really did say was "ill-natured people might be inclined to think" that the omission "was not entirely undesigned on the part of the authors of the circular." Here we have the minor and major premises of a syllogism (in Barbara), and if these are both true the Conclusion must be "Mr. Groves is an ill-natured person." I am sure Mr. Allen would be the first to protest that he had not this in his mind when he wrote his letter. A piece of advice: "Verify your references."

No. 2.—In another part of his letter he says:—"I myself, with scores of others, heard Mr. Groves . . ." Here the vivid imagination comes into play. Mr. Allen pictures himself rising with dignity in the presence of a large and attentive audience to ask the Secretary a question. "Scores of others!" Scores demands two scores at least, it implies a good many scores. Let us look for a moment at the facts. At Dr. Odling's address on the Tuesday there was a good audience, but the next day the attendance was thin, I had almost said meagre; at all events, it was so when I was there. At one time there were 38 people in the room besides the President and Reporter—that makes 40; there might possibly have been one or even two more—that would make 42, and would entitle Mr. Allen to his "scores of others." It is a nicely rounded phrase.

No. 3.—"I myself, with scores of others, heard Mr. Groves state that the papers and discussions at the May Conference would be published in full."

Mr. Allen can of course speak for himself as to what he heard, but is he authorised by the "scores of others" to say what they heard? It is not everyone who is gifted with a vivid imagination. Apparently the unfortunate "shorthand writer" who "attended and took verbatim notes of the discussions" was not. Let us see what this dull, unimaginative person wrote down as the verbatim report of the Secretary's reply to a question put by Mr. Allen (I quote from the shorthand writer's report):—

"The Secretary (Mr. Groves) said that it was not intended to publish the discussion in full."

Your readers will observe that the only difference between Mr. Allen's report of what I said and the shorthand writer's is the word "not;" but its omission slightly alters the sense. My own impression is that the reporter's version is correct.

I might criticise every paragraph, every sentence almost in the same way, but I should weary your readers and have to discuss matters which I did not touch on in my first letter; moreover, it would not be fair to Mr. Allen, for I know that he, at all events, has written his letter in all honesty of purpose. If instead of being like David in his haste he had carefully eliminated everything which was doubtful before sending in that letter, I believe I should have been able to cordially agree with nearly all that was left.

As regards Mr. William Thomson. He tells us it is the printer's fault that a garbled quotation from the Charter was given in the circular bearing his signature. It is very unfortunate that the printer should have omitted the two

words "consulting and," thereby entirely altering the meaning of the quotation. If he had left out one of the two only, the omission would of course have been at once detected by Mr. Thomson when correcting the proof. Except in the list of names, this, however, appears to be free from mistakes, even in the punctuation, although Mr. Thomson apologises as not having had time to revise the proof as carefully as he should have wished. I congratulate him on his skill.

In reference to his assertion that a pledge was given "to publish a full report of the proceedings of the Conference of the Institute," I can only repeat what I have already said, "This statement is—to speak quite plainly—untrue."

Again, Mr. Thomson, fired with virtuous indignation, writes:—"I am sorry Mr. Groves wrote the last paragraph of his letter, because it insinuates sinister motives on the part of gentlemen who, no one could doubt, would fully uphold the integrity and dignity of the Institute."

The paragraph referred to asks the members of the Institute to frustrate the attempt to hand over the Institute to the public analysts (*i.e.*, "members of the Society of Public Analysts").

Your readers will scarcely credit it, but the printing ink on the CHEMICAL NEWS of Feb. 19, in which that paragraph of Mr. Thomson's appeared, was hardly dry when he indited a circular. That circular directs that seventeen names should be struck out of the voting list as sent out by the Council,—in fact, with the exception of five, to eliminate every one of the ordinary members of Council who are not members of the Society of Public Analysts. The new members proposed are all members of the Society of Public Analysts, with two exceptions.

I state the bare facts, and commend them to the consideration of your readers, together with Mr. William Thomson's letter.—I am, &c.,

CHARLES E. GROVES.

Guy's Hospital, Feb. 23, 1892.

P.S., Feb. 24.—Since writing the above Mr. Allen has kindly sent me a copy of his letter (see below). It gives me the greatest pleasure to find that my estimate of his open, honest character is a just one.—C. E. G.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—Mr. Charles E. Groves informs me that he finds on reference to the verbatim report of the proceedings at the May Conference that, in answer to a question put in open meeting whether it was intended to publish a full report of the proceedings, he replied that "it was not intended to publish the discussion in full." I can only express my regret that I and many others misunderstood Mr. Groves's reply, and of course at once accept his disclaimer.

I fail, however, to see that the alteration much improves the position, for it is difficult to understand what justification there could be for spending upwards of £50 in taking verbatim notes of and printing the discussions if it was intended to publish merely an abstract, while even this intention has been abandoned. It appears to me that members of the Institute not able to be personally present at a conference have a right to a full knowledge of the proceedings, especially as a considerable sum of their money was spent in reporting and printing these.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, Feb. 23, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I think a good deal of confusion has arisen in the Institute discussion from a forgetfulness of its early

history. Many of the expressions in the Charter are legacies from the parent society, and should be read by the light of the incidents that gave rise to them.

An outcome of the "black-balling contest" of 1877, the Institute was formed to look after the interests of "chemistry as a profession," in the same way as the Chemical Society is concerned with it as a science. It was called deliberately and comprehensively "The Institute of Chemistry" (and not "The Institute for Analysts").

When the Institute was in embryo we heard only of "committee of chemists," "chemists' organisation committee," "professional chemists," and so forth; but the *Pharmaceutical Society* formally objected to this, and claimed a legal monopoly in the word "chemist" undefined, and a right to prosecute any person not a member of their body who so used it.

Robbed of our birthright by the Pharmacy Act a paraphrase had to be found, and "analytical and consulting chemist" was adopted. This term marked us off sharply from the "chemists" of the Pharmacy Act, and was quite broad enough to cover most professional chemists who cared to join, whether the analytical chemists in works, the analyst pure and simple, or the professor who was open to consultation.

In those days the great idea was to elect on the Council a few representatives of every possible section of applied chemistry, to bind all branches together, and to construct out of these elements a chemical profession that the public could understand.

That was the "elevation" I looked for when, as one of the earliest A.I.C.'s, I joined the Institute—a brigading together for mutual protection of all bonâ fide chemists.

It was also agreed that, however good the training in a private laboratory might be, it was rarely broad enough, and some collegiate education was essential.

I regret very much to find that a section of the society should now be endeavouring to pare down this scheme by a narrow interpretation of phrases forced on us by obstructionists outside our profession.—I am, &c.,

F. WOODLAND TOMS.

Jersey, Feb. 22, 1892.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The victim of misplaced confidence is always interesting. What rogues those printers are, to be sure! and yet how strangely their carelessness and Mr. Thomson's want of time to correct it fit in and aid the Fifty-nine in their attempt to place the Analyst before all.

Thus does chance guide untoward events, printers' errors included.

Of course it was the ink, or the pen, or the paper, or something, which caused the following to appear on p. 2 of the Manifesto:—

"We propose . . . to substitute the names of *Analytical Chemists* in actual practice for those of some of the members nominated on the official list issued by the Council." Or could it have been that careless printer again?

The Council was aware that the refusal to print the discussion of the May Conference would be used against it, but gentlemen able to decide what Council business may or not be treated as an open secret are at least aware that the very best party move that those opposed to Analyst preponderance could have made was to print those speeches as spoken and unedited by the speakers. The majority of the Council, however, considered the reputation of the Institute of more value than a party triumph.

The best antidote to all this exaggerated talk lies in a careful consideration of the *Proceedings*, Part III., 1891, and the "Report of the Council" just issued.

Members who carefully read them and consider the work

done will no doubt so use their ballot papers as not to "disagreeably surprise" the "late" (?) Secretary, but the spokesmen of the Fifty-nine.—I am, &c.,

R. J. FRISWELL.

115, Darenth Road, N., Feb. 22, 1892.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

SIR,—The publication of the letter of your correspondent W. S. on the above subject appears to invite an expression of opinion as to how a Society of Students can best set to work to advance themselves in the Science individually and collectively. There is surely only one answer to your correspondent's questions. Seek first the Science and its discipline and all those things shall be added! A College Society devoted to Science, as the universal and particular milch cow, will only help to swell to the flood of mediocrity, which is threatening to put out the fires of genius for ever!—I am, &c.,

C. O. O.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 6, February 8, 1892.

Silica in Plants.—MM. Berthelot and G. André.—The part played by silica in plants, especially in the Gramineæ, raises interesting questions both physiological and practical. Silica takes part in forming the solid framework of plants, and we may ask if it does not take a certain share in the distribution of the nutrient matters. The authors have determined the absolute and the relative proportions of silica in the grain and in the soil. They have made similar determinations in the plant at successive stages of its growth, from germination to fructification, examining successively each of the essential parts of the plant. They operated upon spring-wheat, determining the silica in four forms: total silica, silica soluble in pure water, silica soluble in cold dilute potassa, and soluble in hot dilute potassa. They have reserved the question whether the silica is absorbed as such (pure) or in combination with carbonic or mineral principles. The soil was a sandy loam in which the silica was entirely present in the state of quartz and of stable silicates. The silica of the grain was almost totally in the state of silica soluble in cold dilute alkalis, its total proportion not reaching 1-100th of the weight of the grain. The total weight of silica is greatest in the root. The relative proportions of silica soluble in water or in dilute potassa are higher in the stem. Here nearly three-fourths of the silica are present in a state insoluble in dilute potassa. Before inflorescence the silica of the stem is almost entirely soluble in alkalis. Leaving out of question the roots, which are more or less contaminated by the soil, the total silica is at its maximum in the leaves. The ear is always the part of the plant least rich in silica.

Determination of the Point of Congelation of Highly Dilute Aqueous Solutions: Application to Cane-Sugar.—M. Raoult.—By means of improvements in the refrigerating mixtures and in the agitators employed, the author has obtained more precise determinations than those detailed in his paper in the *Annales de Chimie et de Physique* (Series 6, vol. ii., p. 93, 1884). For weights of sugar from 0.683 grm. to 39.040 grms. per 100 grms. of water the congelation point falls from 0.042°

to $2'27''$. He is able to determine reductions in the freezing-point down to 1-500th of a degree.

New Researches on the Solar Atmosphere.—H. Deslandres.—The author, referring to his former paper (*Comptes Rendus*, August, 1891) on photographic researches on the solar atmosphere, comprising the blue, the violet, and the ultra-violet up to $\lambda 380$, has now extended his examination of the contiguous part of invisible ultra-violet region as far as $\lambda 350$. He has rediscovered in several of the solar protuberances of the second half of 1891 the series of ultra-violet hydrogen rays detected for the first time by Prof. Huggins in the white stars. He has obtained as many as eight successive brilliant rays all fine and well defined (Mr. Hale had found five of these rays and Prof. Young four), and he does not doubt that at a station on a high mountain the two remaining rays of the series might be detected. Thus the sun, which is a yellow star, presents in certain parts of its atmosphere the characteristic radiation of the white stars. This result confirms our present ideas on the evolution of the stars. He has also obtained a hydrogen ray a little more refrangible than α ($\lambda 388$), noticed for the first time by Hales, and recently contested by Prof. Young.

Action of Chlorine upon Ruthenium; Its Sesquichloride and Oxichloride.—A. Joly.—The chlorination of ruthenium is effected very precisely either at 360° or 440° on heating the finely divided metal in a mixture of carbon monoxide and chlorine, the latter always in excess. The metal is rapidly converted into a br. wn powder and increases considerably in bulk. The sesquichloride, RuCl_3 , is insoluble in cold water and the acids, mineral and organic. Boiling water destroys it slowly; the liquid becomes acid and takes a light blue colour, but the greater portion remains insoluble as a black powder. It dissolves neither in carbon chloride nor disulphide, nor in chloroform, nor phosphorus trichloride, nor ether. If digested for some hours in a sealed tube with 50 parts of absolute alcohol it dissolves slowly, and unattacked ruthenium remains as residue. The alcoholic solution is intensely coloured; in a shallow layer it is of a purple violet, which does not change if preserved in a sealed tube. If exposed to atmospheric moisture, or if the alcohol used as a solvent is alcohol at 95° , it changes in some days to a blue-violet, and then to a deep indigo. This change is most rapid at 60° . The solution in absolute alcohol, if evaporated in a dry vacuum, leaves a brownish residue with bronze reflections. If the blue liquor is distilled it leaves a black product which, if dried in the stove at 150° , has the composition of an oxichloride, $\text{Ru}(\text{OH})\text{Cl}_2$. The oxichloride is very soluble in water, with an indigo blue colour. The liquid is neutral. If diluted it becomes turbid at the ordinary temperature, and deposits a black-brown flocculent precipitate of ruthenium sesquihydroxide, $\text{Ru}(\text{OH})_3$. If the oxichloride is treated in heat with concentrated hydrochloric acid, there is formed a brown solution which turns yellow on dilution. This solution is a hydrochlorate of ruthenium chloride, which at 200° becomes transformed into the anhydrous chloride. At the ordinary temperature soda throws down from solutions of the hydrochlorate, the chloride and the oxichloride, ruthenium hydroxide. Ammonia combines with the oxichloride, forming a product very soluble in water and of the intense red of the alkaline solutions of phenolphthaleine.

On a Silver Nitrosilicate, and on the Existence of a Nitrosilic Acid.—G. Rousseau and G. Tite.—This paper will be inserted at some length.

Lead Chlorosulphide and Bromosulphide.—F. Parmentier.—The compound obtained on precipitating a salt of lead by hydrogen sulphide in presence of dilute hydrochloric acid, has the composition PbS, PbCl . It is of a cinnabar red whilst suspended in water, but after subsiding it becomes darker. It is not stable, being decomposed by water, acids, and alkalis. Alkalis at first

blacken it, and then the black body is rapidly transformed into a white flocculent mass. The bromosulphide, and probably the iodosulphide, are analogous in properties and in composition.

The Decomposition of Sulphurous Acid by Carbon at Very High Temperatures.—M. Scheurer-Kestner.—Sulphurous acid at very high temperatures is decomposed by carbon, forming free sulphur, carbon monoxide, and carbon dioxide. M. Berthelot has shown that at a lower temperature sulphurous acid is converted into carbon monoxide, oxisulphide, and sulphide. The two latter bodies are not permanent at very high temperatures.

A Nitro-derivative of Antipyrine.—Edm. Jandrier.—Nitrodimethoxyquinizine forms straw-coloured crystals insoluble in cold water, and sparingly soluble in boiling alcohol. Its best solvent is glacial acetic acid. On treatment with zinc and acetic acid it yields amido-antipyrine.

The Rotatory Power of the Diacetyltartaric Derivatives.—J. A. Le Bel.—A controversial paper in reply to a memoir by M. Colson, in the *Comptes Rendus* of January 25th. The author argues that stereochemistry is independent of the hypothesis of the tetrahedron.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., No. 12.

On Nitrised Silk.—Leo Vignon and P. Sisley.—The yellow colour obtained by the action of ordinary nitric acid upon silk is best produced with a mixture of nitric acid and water of the specific gravity 1.133 heated to 45° . After washing in excess of water the silk retains a characteristic yellow colour, fast to air and light. Pure nitric acid, free from nitrous products, gives no colour on silk under the above conditions, but if a little sodium nitrite is added the yellow colour comes up. The tone obtained with nitrous-nitric acid is darkened by a passage through alkalis. It is palest with ammonia and reddest with baryta. Silk nitrised is enriched in nitrogen, and impoverished in carbon and oxygen.

Constitution of Solutions of Salts of Chromium Sesquioxide Modified by Heat.—A. Recoura.—The author has met with three varieties of solutions of chromium sulphate:—1. The violet solution containing the neutral sulphate, which, on evaporation, gives the crystalline violet sulphate. 2. The non-crystalline solution resulting from the action of heat upon the former, and containing free sulphuric acid and the basic sulphate. 3. A green, non-crystalline solution, obtained by precipitating chromium oxide from the former solution and re-dissolving in sulphuric acid. It contains the basic sulphate.

Contribution to the History of the Salts of Nickel and Cobalt.—A. Terreil.—This paper will be inserted at some length as early as possible.

Colorimetric Determination of Iron by means of the Sulphocyanide and some other Coloured Combinations of this Metal.—J. Riban.—It is proposed to determine small quantities of iron, especially in the blood, by transforming them into sulphocyanide and comparing the solutions thus obtained with type solutions containing a known weight of the same sulphocyanide. The paper requires the accompanying tables.

The Reaction of Iodine with Acid Sodium Sulphite.—W. Spring and E. Bourgeois.—A controversial paper, having reference to a paper by Prof. Otto, of Brunswick.

On Acid Potassium Tartrate as Original Standard Substance for Acidimetry and Alkalimetry.—Prof. Dr. A. Bornträger.—The author recommends potassium bitartrate, because it forms anhydrous crystals, is very slightly hygroscopic, can be dried at a high temperature, and preserved for an unlimited time.—*Zeitschrift für Analytische Chemie*, xxxi., Part 1.

MISCELLANEOUS.

The University of Dorpat.—Many of our readers will learn with righteous indignation that the Russian Government is preparing for the suppression of the time-honoured University of Dorpat.

Royal Institution.—Professor W. P. Ker will, on Thursday next (March 3), begin a course of three lectures on "The Progress of Romance in the Middle Ages." Mr. F. T. Piggott will deliver his Friday evening discourse on "Japanesque," on March 11th, in place of Professor Oliver Lodge, who will give his lecture on "The Motion of the Ether near the Earth" on April 1st.

MEETINGS FOR THE WEEK.

- MONDAY, 29th.**—Medical, 8.30.
Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).
TUESDAY, March 1st—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30. (Anniversary).
Pathological, 8.30.
WEDNESDAY, 2nd.—Society of Arts, 8. "Spontaneous Ignition of Coal and its Prevention," by Prof. Vivian B. Lewes.
THURSDAY, 3rd.—Royal, 4.30.
Royal Society Club, 6.30.
Royal Institution, 3. "The Progress of Romance in the Middle Ages," by Prof. W. P. Ker, M.A.
Society of Arts, 8. "Indian Sanitation and the International Congress of Hygiene," by Surgeon-Genl. Sir William James Moore.
Chemical, 8. "A Rule for Determining whether a given Benzene Mono-Derivative shall give a Meta Di-derivative or a Mixture of Ortho and Para Di-derivative," by Prof. Crum Brown and Dr. Gibson. "The Relative Orienting Effect of Chlorine and Bromine," by Dr. Armstrong and Mr. Briggs. "Contributions to our Knowledge of the Aconite Alkaloids—Part II. The Alkaloids of True Aconitine napellus," by Prof. Dunstan and Mr. Umney; "Part III. The Properties of Aconitine—Conversion of Aconitine into Aconitine," by Prof. Dunstan and Dr. Pasmore. "Note on the Luminosity of Coal-Gas Flames," by William Foster, M.A.
FRIDAY, 4th.—Royal Institution, 9. "The Surface-Film of Water and its Relation to the Life of Plants and Animals," by Prof. L. C. Miall, F.L.S.
Geologists' Association, 8.
Quekett Club, 8.
SATURDAY, 5th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

ENGLISH TRANSLATION OF MENDELEEF'S
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By D. MENDELEEF,

Professor of Chemistry in the University of St. Petersburg.

TRANSLATED BY

GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg,

AND EDITED BY

A. J. GREENAWAY, F.I.C., Sub-Editor of the Journal of the Chemical Society.

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TUESDAY, MARCH 1, 1892.

Re L. COWAN AND SONS, Limited, Hammersmith Bridge Sugar Refinery, Barnes, London, S.W.

WHEATLEY KIRK, PRICE, & GOULTY

are instructed by the Receiver, J. Milton Broad, Esq., to SELL by PUBLIC AUCTION at the Mart, Tokenhouse Yard, London, E.C., on TUESDAY, MARCH 1, 1892, at Two o'clock prompt, in one lot, the valuable Plot of Freehold Land, with a frontage of 300 feet to the River Thames, including a Timber Wharf of 130 feet, entrance gates and paved road. The buildings include very substantial fireproof factory four storeys high, numerous other erections, stables, retort house, engine and boiler houses, workshops, complete gas works and plant. The premises are suited for any manufacturing purpose. They were recently constructed for a Sugar Refinery; ample land for extensions is included.—Plans and full particulars can be obtained gratis on application to the Receiver, J. Milton Broad, Esq., 1, Walbrook, London, E.C.; Linklater, Hackwood, Addison, and Brown, Solicitors, 2, Bond Court, Walbrook, London, E.C.; H. Montagu, Esq., Solicitor, 5 and 6, Bucklersbury, London, E.C.; and from Wheatley Kirk, Price, and Goult, 52, Queen Victoria Street, London, E.C.; and Albert Square, Manchester.

N.B.—The Plant and Machinery forming the contents of the above works will be Sold piecemeal by Public Auction the day following the sale of the premises; vide Advertisements.

Old Established Soap Factory to be Sold, in one Lot, as a complete going concern.

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Re L. COWAN AND SONS, Limited, Hammersmith Bridge Soap Works, Barnes, London, S.W.

WHEATLEY KIRK, PRICE, & GOULTY

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WEDNESDAY, 2nd, and THURSDAY, 3rd MARCH, 1892.

Re L. COWAN AND SONS, Hammersmith Bridge Sugar Refinery Barnes, London, S.W.

WHEATLEY KIRK, PRICE, & GOULTY

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THE CHEMICAL NEWS.

VOL. LXV., No. 1684.

ON A SILVER NITRO-SILICATE, AND ON THE EXISTENCE OF A NITRO-SILICIC ACID.

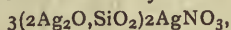
By G. ROUSSEAU and G. TITE.

No silver silicate has hitherto been obtained. The experiments of Stas tend to prove that finely divided silver combines with glass heated in a current of air to near its softening point. But the quantity of metal which thus passes into the state of silicate is too slight to warrant the conclusion of the existence of a compound of silver and silica in definite proportions.

The researches about to be described seem to throw some light on this question. They have terminated in the discovery of a complex salt containing silica, nitric acid, and silver oxide.

Although the formation of a basic silver nitrate seemed, from analogy, scarcely probable, we heated in sealed tubes a mixture of 1 mol. of silver nitrate, with from 1—2 mols. of water, in presence of fragments of marble. Up to 180° no insoluble compound was separated out, but the liquid took a pale yellow colour. From 180° and as far as 300° and upwards, we obtained crystals of a ruby-red colour, which adhered strongly to the tubes. They are formed slowly, especially at about 200°. To obtain a practical yield the experiment must be prolonged for sixty hours. The product is always mixed with crystalline tablets of silver carbonate, which are easily separated by levigation.

The composition of the red crystals is—



representing a compound of silver silicate and nitrate. But on more careful study it appears that the compound must be regarded as the silver salt of a nitro-silicic acid, $7\text{Ag}_2\text{O}, 3\text{SiO}_2, \text{N}_2\text{O}_5$.

The silica is derived from the action of the solution of silver nitrate upon the glass of the tubes. Hence, the crystals obtained in these circumstances are strongly attached to the sides, whence it is often difficult to dislodge them. If we take care to add previously to the mixture of water and silver nitrate a little dry silica, obtained from the decomposition of silicon fluoride by water, we obtain crystals which no longer adhere to the glass.

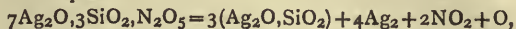
In order to avoid the formation of silver carbonate we have sought to substitute for the marble either finely-divided silver or silver oxide. In presence of metallic silver the neutral nitrate remained unaffected. Silver oxide gives us better results, on condition of not exceeding the temperature of 200°, but it is always difficult to separate the excess of oxide from the silver nitro-silicate.

We finally succeeded in reproducing this compound by mixing silica, dried at 100°, with dry silver nitrate, kept for some hours in fusion in a crucible of the same metal at temperatures of from 350—440°. The crystals thus obtained in the dry way are much smaller than those formed in sealed tubes in consequence of the greater rapidity of their formation.

Silver nitro-silicate appears in the form of short prisms of a ruby-red colour when seen by transmitted light, if sufficiently thin and presenting longitudinal extinctions in parallel light. When thicker they become opaque, and appear then of a bluish-black by reflected light.

If heated to dull redness these crystals melt, with intumescence, giving off nitrous vapours. The residual white, porous mass resulting from the ignition seems to

contain reduced silver and an acid silicate, $\text{Ag}_2\text{O}, \text{SiO}_2$. The conversion of the original substance into silicate, metal, and nitrous vapours seems to take place according to the equation—



corresponds in fact to a loss of 9 per cent of the theoretic weight. In two experiments we found 8·86 and 9·08, values which agree with moderate exactness. On the other hand, the residue is attacked by the nitric acid with effervescence, and the escape of nitrous vapours, which indicates the presence of metallic silver in the mixture.

Silver nitro-silicate is easily soluble in dilute nitric acid; the solution, clear at first, becomes turbid if concentrated on the water-bath, in consequence of the formation of a deposit of silica. Hydrochloric acid decomposes it instantly, producing silver chloride. We sought to isolate the nitro-silicic acid liberated in this reaction. In contact with a solution of ammonium hydrochlorate the silver salt is destroyed; the liquid takes a strongly alkaline reaction and exhales a decidedly ammoniacal odour. The liquid if filtered to remove silver chloride, and then concentrated in a vacuum, leaves a residue of gelatinous silica.

Potassium chloride in solution seems to be without action even at the temperature of 100°. If it is moistened with a solution of potassium iodide the nitro-silicate at once takes the yellow tint of silver iodide. If we mix the silver salt and the alkaline iodide in the proportion of 1 equivalent of the former to 7 equivalents of the latter, all the silver is separated as an iodide. The filtrate, if evaporated *in vacuo*, leaves long, colourless needles of potassium nitro-silicate.

In a subsequent communication we shall give the composition and the properties of the alkaline nitro-silicates obtained in this manner.—*Comptes Rendus*, vol. cxiv., p. 291.

NOTE ON THE ESTIMATION OF NITROUS ACID.

By ARTHUR G. GREEN and F. EVERSLED.

We have recently had our attention called to an article by Prof. Lunge on "The Estimation of Nitrous Acid in Sodium Nitrite" in the November number of the *Zeitschrift für Angewandte Chemie*. In this paper Prof. Lunge makes a critical comparison of the accuracy of various methods which have been proposed, and comes to the conclusion that his modification of the permanganate process is the most accurate.

That his method gives good results when organic matter or other reducing substances are absent we do not doubt, but a method in which these sources of error need not be taken into account is surely to be preferred. Such a method was published by us in 1886 in the *Journal of the Society of Chemical Industry* (vol. v., p. 633), and has since been in constant use in at least one large technical laboratory with satisfactory results. It depends upon the diazotisation of a normal solution of aniline hydrochloride, using starch and zinc iodide as indicator. Prof. Lunge mentions the diazotisation method, but attributes its publication to Boeckmann, stating that it was improved by Schultz (by substitution of sulphanilic acid for aniline), but both these publications were long subsequent to ours. In his examination of the diazotisation method (Schultz's modification) Prof. Lunge arrived at results which were more than 8 per cent too low, and accordingly dismisses the diazotisation method (whether with sulphanilic acid or with aniline) as being entirely inaccurate, expensive, and troublesome, and he considers it should be abandoned altogether. If Prof. Lunge had followed our directions, instead of employing the modification of Schultz, he would probably have arrived at a different conclusion, for in the above mentioned paper we have clearly shown that if aniline hydrochloride is used and proper precautions are taken the method gives results which are sufficiently con-

cordant amongst themselves and only about 0.4 per cent lower than those obtained by Kinnicut's method, which Prof. Lunge approves.

According to our experience, sulphanilic acid (used by Schultz), owing to the slowness of the reaction, is not nearly so suitable for the estimation of nitrous acid as aniline hydrochloride; even with aniline sulphate the reaction is far slower than with the hydrochloride. It is also important to work with tolerably strong solutions, as the more dilute the solution the slower is the reaction.

The following is the method of procedure we employ:—A normal solution of aniline hydrochloride is prepared by dissolving 93 grms. of pure dry aniline, together with 450 c.c. of hydrochloric acid (about 31 per cent HCl), in 1 litre. Of this solution 25 c.c. is placed in a small stoppered bottle surrounded with ice and water, and is titrated with the nitrite solution (made up about normal) with constant agitation. From time to time a drop is taken out and mixed on a white plate with a drop of zinc iodide and starch solution until a blue colour indicates the presence of an excess of nitrous acid. When a slight excess of nitrous acid still remains after the contents of the bottle have stood for an hour, the end-point is reached. In testing with the starch solution account must only be taken of the blue colour which is produced *at once*, as the drop usually turns blue after standing for some time.

ON THE ACTION OF CERTAIN LIQUIDS ON ALUMINUM.*

By Professor GEORGE LUNGE, Ph.D.

SOME months ago a paper was published in a German pharmaceutical journal by Lübbert and Roscher on the behaviour of aluminum toward a number of liquids with which that metal might come into contact when made into canteens, cooking vessels, surgical instruments, &c. The conclusions reached by those two observers would be detrimental to the application of aluminum for any use in which it may come into contact with liquids intended to pass into the human body. Before such a conclusion, momentous as it would be for the extension of the use of aluminum in many directions, can be accepted as valid, it ought to be verified by other observers, especially as neither of the above-named gentlemen is a chemist in the proper sense, one being a medical man and the other a pharmacist fresh from his studies.

The method employed by Lübbert and Roscher is anything but trustworthy. In the first instance they did not make any quantitative estimations, but confined themselves to qualitative observations, which may be very deceptive, as some of the substances employed were probably not free from alumina; secondly, they worked exclusively with aluminum foil, which is well known to be much less resisting to chemical action than compact sheet aluminum.

This induced me to take the matter in hand, in conjunction with my demonstrator, Mr. Ernst Schmid, and I will now give a short account of our results:—

Our experiments were all made with commercial rolled sheet aluminum, 1 m.m. thick, from the Neuhausen works, of the following composition:—0.44 per cent combined silicon, 0.11 per cent crystallised silicon, 0.25 per cent iron; traces of copper; 99.20 per cent aluminum (by difference). The sheet was cut up into strips of such a size that they could be conveniently introduced into the flasks serving for our experiments. Each strip was freed from sharp edges by a file, and was thoroughly cleaned in order to lay bare a real metallic surface and remove the excessively compact surface produced by the rolling process. They were for this purpose treated, first with concentrated solution of caustic soda, then with water,

then with dilute sulphuric acid, again with water scrubbed with a brush and distilled water, rinsed with alcohol, and dried in an oven. Three such strips were accurately weighed, hung by means of small holes upon a glass hook in such manner as not to touch one another, and introduced into the flasks containing the liquids to be tested. Each flask held about 400 c.c. of liquid, and was closed by a cork through which passed the stem of the glass hook. After leaving the whole for six days at the ordinary temperature of the room, the strips were taken out, rinsed with distilled water, freed from any adhering alumina by means of a soft brush, rinsed with alcohol, dried, and weighed. The loss of weight was referred to the aggregate surface of the three strips (about 130 square centimetres), and is in the following table reduced to 100 square centimetres. Each liquid was tested at least twice in order to guard against accidental mistake. In a few cases, where the nature of the liquids presented no special difficulties, the alumina was, moreover, determined gravimetrically in the liquid after the experiments with results closely approximating those found by ascertaining the loss of weight of the aluminum. The following table gives the results of our experiments.

Liquids experimented upon.	Loss in weight.			
	A. M.g.	B. M.g.	Average. M.g.	Reduced to a surf. of 100 sq. cm. M.g.
Ordinary claret	4.1	3.3	3.7	2.84
" hock	4.0	4.5	4.3	3.27
Brandy	1.6	1.2	1.4	1.08
Pure 50% alcohol	0.8	0.8	0.8	0.61
5% solution tartaric acid	1.9	2.4	2.2	1.69
1% " " " " " "	3.6	3.1	3.4	2.58
5% acetic acid	4.3	5.7	5.0	3.85
1% " " " " " "	6.2	5.2	5.7	4.38
5% solution of citric acid	2.8	2.8	2.8	2.15
1% " " " " " "	2.3	2.6	2.5	1.90
5% lactic acid	6.1	6.3	6.2	4.77
5% butyric acid	1.7	1.7	1.7	1.31
Coffee	0.6	0.7	0.7	0.50
Tea	0	0	0	0
Beer	0	0	0	0
4% boric acid solution ..	2.3	2.3	2.3	1.77
5% carbolic acid	0.1	0.5	0.3	0.23
1% " " " " " "	0.8	0.5	0.7	0.49
1% salicylic acid	7.3	9.2	8.3	6.35

In very few of the cases was any action outwardly visible. In the case of brandy and alcohol, where the quantitative action was extremely slight, the surface of the aluminum showed a few fungus-like excrescences, probably formed by alumina and caused by accidental flaws in the sheet. Lübbert and Roscher found that alcohol, ether, and all similar liquids had no action at all on aluminum foils, so that the observation made by us would appear to be due to an accidental cause. Only in the last case, that of a solution of salicylic acid, did the aluminum lose its bright surface and become dull.

From our experiments the following conclusions may be drawn:—The action of coffee, tea (both of which had been poured in hot), and beer is zero, or practically so; that of brandy is also extremely slight; the action of acids and acid liquids (wine, sour milk, fruit-juices, &c.) is more pronounced, but even in this case far too slight to cause any alarm whatever. Taking the worst case found, that of acetic acid, we find a maximum attack of less than 5 m.grms. per 100 square centimetres in six days. Now a canteen holding a litre (or nearly a quart) has an inner surface of about 600 square centimetres and an aluminum weight of about 200 grms. Such a canteen would in the very worst case lose 5 m.grms. in a day, even if it were always full, or 1 gram. in two hundred days, and only in fifty-five years would it be reduced to half its weight. This is certainly too trifling a work to be

* Engineering and Mining Journal.

practically considered. Nor is there the slightest danger of any injurious action upon the human body by such traces of aluminum compounds, seeing that our food contains very much more of these. Moreover, aluminum compounds are not poisons in the ordinary sense to be compared to compounds of arsenic, mercury, lead, copper compounds, &c.; they cannot act injuriously unless quantities a hundred times larger than those we have found were regularly entering into the human stomach.

The final conclusion must, therefore, be this: that aluminum may, without any fear, be employed for canteens or any other vessels serving for holding articles of food at least at the ordinary temperature.

REPORT ON DETERMINATION OF NITROGEN.*

By E. B. VOORHEES.

(Concluded from p. 100).

Kjeldahl Modified for Nitrates.

Remarks.—The average of the results reported on sample No. 1 is 13.91; excluding two that report much less nitrogen than the sample is shown to contain, the average is 13.96, or 0.05 of 1 per cent less than the calculated percentage.

On a basis of an average of 13.96 per cent, nine chemists are within one-tenth of 1 per cent, the limit usually allowed for experimental error; thirteen chemists, or 65 per cent of the whole number, are within 0.15 of 1 per cent, the limit often allowed between duplicates; twenty chemists, or the whole number included in the average, are within 0.3 of 1 per cent, the limit of error allowed by commercial chemists for what is termed "factory work."

The average of the results on sample No. 2 is 7.81; if we exclude one which is evidently much too high, and one too low, the average remains the same, and is 0.15 of 1 per cent less than the calculated percentage. Eight chemists are within 0.1 of 1 per cent of either the calculated per cent of 7.96 or the average per cent secured of 7.81. Taking 0.2 of 1 per cent as the limit of error, eleven chemists are within the same on the basis of the calculated per cent, while on the basis of the average secured sixteen are within the limit. Inasmuch as more than half the whole number of results reported on this sample are lower than the average of 7.81, the result above noted would seem to indicate either that the calculated per cent was too high or that on a mixture of this character the results secured by the official method are too low. While sample No. 2 is an unusual mixture and somewhat difficult to manage, I am of the opinion that the trouble is not with the method.

If we simply compare the average of this year with that of last year, the results by the modified Kjeldahl show no apparent improvement, yet the fact that the average this year represents the work of twenty-four experiment station chemists, some of whom are reported to be inexperienced, as against fifteen chemists last year, which number included commercial chemists of high standing, it indicates a slight improvement in the work, and seems to me to fully verify the statement made by Mr. Scovell in his report for 1889, viz., "that the modified Kjeldahl method is an accurate and reliable one for the determination of nitrogen in fertilisers containing nitrates."

Kjeldahl Method.

The average of the determination reported on sample No. 3 is practically identical with the calculated percentage. Ten chemists are within 0.1 of 1 per cent of the average, and the difference between the highest and the

lowest is but 0.43 of 1 per cent, a result which is highly satisfactory.

Alternate Methods.

The results on Nos. 1 and 2, by both the "Ruffle" and absolute methods, are lower than by the official, though a fair comparison cannot be made owing to the very few reports by these methods. The soda-lime method gave results practically identical with those secured by Kjeldahl.

In accordance with the recommendations made by the reporter in 1889 the chemists of the Kentucky Station reported results secured on official samples Nos. 1 and 2 by substituting for 2 grms. of zinc dust and 2 grms. of salicylic acid, 2 grms. of zinc sulphide and 1 gm. of salicylic acid.

Results.

Analysts.	Per cent nitrogen.		
	No. 1.	No. 2.	Potassium nitrate, C. P.
M. A. Scovell	14.08	7.99	—
A. M. Peters	—	7.82	13.79
H. E. Curtis	13.99	7.76	—
Theoretical	14.01	7.96	13.83
Average association results	13.96	7.81	—

The above results are the averages of several determinations agreeing closely with each other.

A practical test of this method was also made at the New Jersey Station, where thirty-three samples of commercial fertilisers containing nitrate nitrogen, ranging from 0.1 to 2.62 per cent, were duplicated by the official Kjeldahl for samples containing nitrates and by the suggested modification.

2 grms. salicylic acid and 2 grms. zinc dust.	1 gm. salicylic acid and 2 grms. zinc sulphide.	2 grms. salicylic acid and 2 grms. zinc dust.	1 gm. salicylic acid and 2 grms. zinc sulphide.
3.51	3.63	3.22	3.31
3.51	3.59	1.85	1.83
2.53	2.50	4.12	4.09
4.21	4.24	1.10	1.06
4.36	4.32	1.45	1.39
3.03	2.91	2.91	2.85
3.97	4.03	3.31	3.31
2.69	2.78	1.32	1.24
2.22	2.17	1.25	1.31
3.03	3.00	2.82	2.78
4.55	4.56	3.16	3.04
3.54	3.62	2.80	2.74
4.96	4.94	2.41	2.38
3.03	2.99	4.56	4.56
2.69	2.70	3.42	3.34
4.21	4.26	3.18	3.30
4.06	4.07	3.13	3.08
1.90	1.88		

The results were highly satisfactory. The difference in duplicates ranged from nothing to 0.12 of 1 per cent, with an average difference on the whole number of 0.02 of 1 per cent.

Errors Due to Reagents.

A few chemists reported difficulty in securing uniform results on sample No. 1 when different weights were used and the proper deduction made for error due to reagents. This is an important point and should be carefully noted in the study of methods. Mr. Woods, of the Storrs Station, says that "Kjeldahl modified has in blank determinations always given some nitrogen. Should not be surprised at this if it were not that we always obtained about the correct percentage of nitrogen in nitrates (pure salts) without the use of the correction thus obtained, and the results have always been too low when the correction has been used." His report on this point is of considerable value and is appended in full.

* From the *Proceedings of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.*

Modified Kjeldahl Method.

Mean of four "blanks" gave nitrogen corresponding to 0.4 c.c. of ammonia solution, equal to 0.0012 grm. nitrogen.

With potassium nitrate (theory), 13.84 per cent; mean by Tiemann-Schultze method, 13.75 per cent nitrogen.

Per cent nitrogen.	
Without correction.	With correction.
13.75	
12.78	
13.76	
13.68	
Average ..	13.74
	13.27

Nitrogen in Samples.

(Percentages calculated on water content at receipt).

No. 1.		
Per cent nitrogen.		
Tiemann-Schultze method.	Modified Kjeldahl.	
	Without correction.	With correction.
14.03	14.05	
14.08	14.01	
14.16	14.06	
14.19		
Average ..	14.09	13.57

No. 2.		
Modified Kjeldahl method.		
Without correction.	With correction.	
Per cent nitrogen.	Per cent nitrogen.	
7.92		
8.02		
7.96		
7.98		
8.00		
Average	7.97	7.85

The work of Mr. Woods verifies the experience of the New Jersey Station, where the error due to reagents had previously been shown to be equivalent to 0.0010 grm. nitrogen, and which had produced widely varying results on pure nitrates when the proper deduction had been made for different weights taken, the results being invariably from 0.2 to 0.5 of 1 per cent low when less than half a grm. of the material was taken. The following determinations on sample No. 1 were made to illustrate this point.

Weight taken.	Without correction.	With correction.
Grm.	Per cent.	Per cent.
0.9	13.93	13.82
0.8	14.05	13.92
0.7	14.12	13.98
0.5	14.06	13.86
0.5	14.04	13.84
0.5	14.11	13.91
0.4	14.04	13.79
Average ..	14.05	13.87

The average of the four determinations on one-half grm. or less without correction is 14.05; with correction it is 13.85, or 0.20 of 1 per cent less; the average of the three without correction on more than one-half grm. taken is 14.03; with correction 13.91, or 0.12 less.

It seemed reasonable to infer from this work that the results secured without the deduction for error were nearer to the truth, and hence they have been used in the report rather than the others. Further blank determina-

tions were made with proper precautions at our station, and it was shown that our assumed error was too great, since the variations in the results ranged from an equivalent of 0.0002 grm. nitrogen to 0.0010 grm.; in all cases within the limit of experimental error.

Recommendations.

I would recommend that the present official methods be continued for the coming year, but modified to include the use of 2 grms. of zinc sulphide and 1 grm. salicylic acid, instead of the 2 grms. zinc dust and 2 grms. salicylic acid, where duplicate determinations of nitrogen are made in fertilisers containing nitrates. My reasons for this are as follows:—

1. The results reported by this method are quite as satisfactory as by the official method.

2. The zinc sulphide can all be added at once, and is, therefore, much less troublesome than the zinc dust.

3. The oxidation is more rapid, and owing to the fact that less salts are present the distillation is more quiet.

I would suggest, not as an improvement of the official methods, but in order to facilitate work and save expense, (1) that the digestion and distillation be performed in the same flask; (2) that metallic mercury be used instead of the mercuric oxide.

ILLUMINATING FLAMES.*

By Prof. VIVIAN B. LEWES, F.I.C., F.C.S.

FLAME has always had an attraction for us which has been rivalled by few other natural phenomena; and whether we look back to the times when the old Fire Worshipers treated it as a deity, or take the present century and trace the work which has been done and the discussions which have been held as to its cause, and the actions which render it luminous or destroy its light-giving power, we are fain to admit that a subject which has drawn to it so much attention for upwards of twenty centuries must be a worthy object for research, until such time as we have mastered every detail that bears upon the subject. It is upon flame that we have, up to the present, always depended for artificial illumination; and whether that flame has been derived from the torch, the rushlight, candle, oil-lamp, or coal gas, it has played a part second to none in our domestic comfort; while with the birth and development of coal gas in the early years of this century, flame became an important commercial factor in the history of the country. It was not until the waning years of the last century that Lavoisier's historical researches upon combustion gave us the key to the action which leads to the formation of flame; and since that time its history has teemed with important researches, and still more important applications, which have to-day borne fruit in the improvements we see on every side in our methods of utilising flame for both heating and illuminating purposes.

Flame, be it luminous or non-luminous, is produced by the combustion of gaseous matter; and a moment's consideration will render this clear to our minds. Take a piece of Wallsend or Silkstone coal and note how it burns on the hearth,—first swelling and giving out tarry vapours, which ignite and form jets of flame; and these, encircling the coal, carry on the action, and give us the bright mass of flame which renders our English hearth so cheery a companion. On the other hand, take the coke which is derived from this same coal by its destructive distillation in the gas-retort, and watch the clear coke fire as it burns. Here you have no flame of the kind given by the coal, but simply the glowing mass of fuel, with, at most, a small blue lambent flame playing over its surface.

* A Lecture delivered at the London Institution, February 18th.—From the *Journal of Gas Lighting*.

What is it that has happened during the conversion of the coal into coke which made so great a difference in its method of combustion? If we analyse the coal and then the coke formed from it, we can at once trace the cause which has given us in the one case flame and in the other none:—

	Silkestone coal.	Coke from Silkestone coal.
Carbon	79.0	89.0
Hydrogen . . .	5.2	1.0
Nitrogen .. .	1.5	1.0
Sulphur .. .	1.5	1.2
Moisture .. .	4.0	1.2
Ash .. .	2.8	5.2
Oxygen .. .	6.0	1.4
	100.0	100.0

The conversion of the coal into coke has been accompanied by the elimination of hydrogen, which, partly free and partly in combination with carbon, has been driven off, and has formed the coal gas; and with the destruction of the constituents capable of forming gas the property of burning with flame has disappeared. Again, take a piece of pine-wood and ignite it. Its combustion will be marked by a large and luminous flame; while after conversion into charcoal, by elimination of its gas-producing constituents, it burns with a flameless combustion. From such experiments as these we are forced to the conviction that flame is gas or vapour undergoing combustion; and inasmuch as combustion is chemical combination, we can define flame as being gaseous matter undergoing active chemical combination.

In all the earlier experiments with flame and with the other phenomena of combustion, it was only those substances which ordinarily burnt in air that were studied and experimented with,—those bodies which would burn in air being called combustibles; while oxygen and air were looked upon as supporters of combustion. This conventional limitation of the processes of combustion still exists. A little reflection, however, shows us that such terms must be purely relative; as, if flame depends merely upon active chemical combination taking place between gases, it can only exist where both the combining gases are present, and it cannot matter which of them has the credit of being the combustible, as a jet of air or oxygen will burn just as well in an atmosphere of coal gas or hydrogen as the hydrogen or gas would in air.

It might be imagined that, having come to these conclusions with regard to flame, it would be a comparatively simple matter to solve the other problems connected with it; but on studying the subject it is at once found that the physical and chemical actions taking place are of the greatest complexity, and are in many cases governed by laws of which we know but little. In the propagation of flame, for instance, the combination of the inflammable constituents at the first moment of combustion gives rise to a great increase in temperature, which in many cases is sufficient to check and alter the combination, and in some instances even to cause dissociation of the products formed in the earlier phases of combustion; so that the combination seems to take place in waves, and not evenly, as one might at first imagine, with the result that the maximum temperature of a flame is never so great as one would expect from calculations based on the heat of combustion of the gases and the specific heat of the products and residual nitrogen from the air. These points, together with the rate of propagation and burning of gases, have been the subject of historical researches by Bunsen, Déville, Berthelot, and others; but much still remains to be done before we arrive at any final conclusion on the subject.

By far the most interesting, and at the same time important, chapter in the history of flame, however, is the consideration of the causes which lead to the luminosity of those flames upon which we depend for most of our

domestic lighting; and these offer so beautiful a field for both physical and chemical research that they have attracted the attention of many observers, and form no inconsiderable addition to the chemical history of this century. In the year 1816, while engaged upon those celebrated researches which culminated in the discovery of the miner's safety-lamp, Sir Humphry Davy noticed certain facts which led him to work out and propound his theory of the causes which lead to luminosity in flame,—a theory which is generally stated as being that the presence of solid particles in the flame is essential to its luminosity. This theory remained unquestioned until 1868, when Prof. E. Frankland, in his celebrated communication to the Royal Society, showed that, although incandescent solid matter in a flame renders it luminous, luminosity is also in many cases produced when the flame contains very dense vapours at a sufficiently high temperature, and also that a non-luminous flame may be rendered luminous by increasing the pressure.

This gave rise to a storm of criticism, and the next few years drew forth a rich crop of papers on the subject. Prof. Frankland not only showed that flames might be luminous without containing solid particles, but advanced the theory that the luminosity in the flame of a burning gaseous hydrocarbon was due to dense hydrocarbon vapours, and pointed out that the soot deposited upon any cool substance held in such a flame contained hydrogen. To this W. Stein replied, showing that the deposited soot contained less than 1 per cent of hydrogen, which was therefore probably only occluded by the carbon; and also that, if it had been present as a vapour in the flame, it ought, on being heated to the same temperature as the flame, to be once again volatile, which it undoubtedly is not. In the year 1874, Soret attempted to show that the cause of luminosity in flame really does depend upon the presence of solid particles by focussing the sun's rays upon a luminous flame, and examining the reflected light by means of a Nicol prism; and rather later Burch pursued the same line of research, but employed the spectroscope for his examination of the reflected light. Their results point unmistakably to the presence of solid particles; and at the present time I think there is very little doubt in anyone's mind that, as far as the flames of candles, oil, and gas are concerned, Sir Humphry Davy's theory is the correct one. Indeed, I am strongly of opinion that, although in certain points Davy went a little too far in his theory, had he been still among us we should have found that, in his own mind, he applied his theory more especially to the flames of our ordinary illuminants, as in his original memoir he speaks of "common flames," and distinctly says that "when in flames pure gaseous matter is burnt, the light is extremely feeble," and again, "the intensity of the light of flames depends principally upon the production and ignition of solid matter."

While this war of solid particles *versus* dense vapours was raging, Hilgard, Landolt, Blochmann, and Heumann were trying to trace the chemical actions taking place in various flames, and the causes which led to loss of luminosity when air was mixed with coal gas before combustion in the Bunsen burner. Heumann added the further proof to the "solid particle" theory of luminosity, that all flames which owe their luminosity to incandescent solid matter give definite shadows, while those in which luminosity is due to dense vapours give none; and that candle, oil, and gas flames all cause well-defined shadows.

This brings the work done upon the cause of luminosity down to the present time. The accepted description of a luminous flame now is that it consists of several zones,—an inner one, in which no combustion is taking place; a central one, in which, either by selective combustion or by direct decomposition by heat, carbon or very dense hydrocarbons are liberated, and, being heated to incandescence at the moment of production by the combustion of other gases present in the flame, give it luminosity;

and an outer one, which consists of the products of combustion and atmospheric air heated to incandescence, and in which combustion is complete.

The work of Soret, Burch, and Heumann proves beyond doubt that our ordinary illuminating flames contain in the luminous zone particles of solid matter; and the only solid which could be present is carbon, either pure or containing the merest trace of hydrogen. The chief question now remaining to be solved, consequently, is the action taking place which leads to the formation of the solid particles in the luminous zone of the flame. During the last two years I have devoted a very considerable amount of time and attention to the study of this subject, and I think I have found the key to this important problem,—important from a practical point of view, because, until it is thoroughly solved, all efforts to improve our illuminating gases and the burners in which we consume them can only be the outcome of experiments made without definite idea of the means to employ in order to obtain the results we desire.

Coal gas is a mixture of hydrocarbons with hydrogen and small quantities of carbon monoxide, and it also contains traces of carbon dioxide, nitrogen, and oxygen. The gas manager, however, does his utmost to eliminate the last three, which, if present in anything but the merest traces, would seriously injure the illuminating value of the gas. An analysis of the South Metropolitan Company's gas gives the following as its composition:—

Hydrogen	57'08
Hydrocarbons—	
Unsaturated (containing 0'035 p.c. acetylene)	4'38
Saturated	33'99
Carbon monoxide	2'63
Carbon dioxide	0'79
Nitrogen	0'96
Oxygen	0'15
Bisulphide of carbon	0'02
	100'00

The unsaturated hydrocarbons consist of ethylene, benzene, propylene, butylene, and acetylene, and probably also traces of crotonylene and others; while the saturated hydrocarbons consist chiefly of methane, with traces of ethane, propane, and butane.

Analyses made by Landolt of gases withdrawn from various parts of a luminous coal gas flame, and also a long series of analyses which I have made show that as the gas leaves the burner the hydrogen is the first to be consumed; and that, in the passage up the non-luminous part of the flame, the carbon monoxide largely increases in quantity, while at the same time the methane rapidly decreases, and the unsaturated hydrocarbons seem to be the least affected. In the luminous zone the unsaturated hydrocarbons rapidly disappear, while the carbon monoxide formed in the inner zone, and also the residual hydrogen and methane, undergo combustion. Professor Smithells, in a paper read before the Chemical Society in December last (*Journal of Gas Lighting*, p. 68), also proved that during the incomplete combustion taking place in the inner cone of a Bunsen flame, this same increase in the amount of carbon monoxide was to be observed. The fact that the decrease in quantity of the unsaturated hydrocarbons was but slow in the inner zone, and then took place with considerable rapidity in the luminous zone, favoured the theory that they were broken up by heat in that portion of the flame and liberated the carbon, which, by its incandescence, gave the luminosity. But it does not seem to have occurred to anyone to try to determine whether the unsaturated hydrocarbons at the top of the non-luminous zone were of the same description as those of the coal gas.

It is a matter of common observation that the checked combustion of a luminous flame at once gives rise to the escape of acetylene, and also that, if a Bunsen burner

catches light at the bottom, large quantities of acetylene are formed, of which the presence is at once detected by its distinctive and pungent odour. These facts suggested the idea that, in the inner cone of the flame, acetylene might be formed by decomposition of the original hydrocarbons; and experiment at once showed this to be the case. Of the unsaturated hydrocarbons present in coal gas, 0·8 per cent consist of acetylene; while at the top of the non-luminous zone of a flat flame produced from the same gas, between 80 and 90 per cent of unsaturated hydrocarbons present consist of acetylene; and in all the other luminous flames experimented with the same action was found to take place.

On taking the most important hydrocarbons present in the coal gas, mixing them with about 20 per cent of air, and passing them through a tube heated to the temperature existing near the top of the inner non-luminous zone, the following results were obtained:—Methane gave rise to unsaturated hydrocarbons, acetylene, and carbon monoxide; ethylene gave acetylene and carbon monoxide; hydrogen charged with benzene vapour gave the same; and ethane gave unsaturated hydrocarbons, acetylene, and carbon monoxide. These experiments clearly show that in the inner non-luminous zone of the flame, the heat generated by combustion of the hydrogen of the coal gas in the presence of the small proportion of air drawn into the flame at this point, causes the conversion of the hydrocarbons present in the gas into acetylene and carbon monoxide.

Acetylene is a clear colourless gas, with a strong and disagreeable odour. It consists of 24 parts by weight of carbon, combined with 2 parts by weight of hydrogen. It is one of those bodies which, during their formation, take in heat instead of giving it out; and it is therefore called an "endothermic" compound. Such substances are especially liable to decomposition, as this is accompanied by a rise in temperature instead of, as is the case with most decompositions, an absorption of heat. Acetylene is decomposed at a bright red heat into carbon and hydrogen, together with traces of tarry matter as well as ethylene; while Berthelot has shown it to be so unstable that it can be broken up into carbon and hydrogen by detonating a percussion cap in it.

These important points being established, it is necessary to ascertain if the temperature existing in the various parts of a flame give any clue to the actions going on within them. The beautiful platinum and platinum-rhodium thermo-couple devised by M. Le Chatelier, and introduced to us by Mr. W. Chandler Roberts-Austen, gives a means of measuring the temperatures of flames with an ease and comparative accuracy which was never before hoped for. I made a small thermo-couple of platinum and 10 per cent of rhodium, platinum wire, using it as thin as possible to reduce errors from loss of heat by conduction, and keeping the wires of considerable length to prevent any chance of rise of temperature introducing conflicting currents at the connections with the galvanometer wires. A reflecting galvanometer was employed, and sufficient resistance was introduced into the circuit to keep the spot of light upon the scale at the highest temperature of the flame; and the scale was then graduated for temperature by taking water at 0° and 100° C., and checking the higher temperature by the fusing-points of the chlorides of the alkalies and alkaline earths, as determined by Dr. Carnelley.

(To be continued.)

A New Thermometer Scale.—F. Salomon (*Zeit. fur Angew. Chemie*).—In this scale the initial point is -273° C., the so-called absolute zero, the freezing-point of water = 100, the intermediate space being divided into 100 equal parts. The writer, like the *Chem. Zeit.*, points out that the proposed new scale has great defects, whilst its alleged advantages are partly unimportant and partly altogether illusory (1° S = $2\cdot73^{\circ}$ C!).—*Zeit. Anal. Chemie*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

February 18th, 1892.

Professor W. A. TILDEN, F.R.S., Vice-President, in the Chair.

It was announced that the following changes in the Council were proposed by the Council:—

As Vice-Presidents: Mr. A. Vernon Harcourt, F.R.S., and Professor W. Ramsay, F.R.S., *vice* Professors G. Carey Foster, F.R.S., and J. Emerson Reynolds, M.D., F.R.S.

As ordinary members of the Council: Professor Harold Dixon and Messrs. R. J. Friswell, John Heron, and W. P. Wynne, *vice* Dr. E. Atkinson, Professor E. Kinch, Mr. Boverton Redwood, and Professor Thomas Purdie.

Messrs. Holland, Crompton, Bernard Dyer, and T. S. Dymond were appointed to audit the Society's accounts.

Certificates were read for the first time in favour of Messrs. Alexander Barratt, Bronhenlog, Mostyn, N. Wales; Frank Comyns, B.A. 55, South Street, Durham; Joseph Davies, 28, Roberts Road, Anfield, near Liverpool; James C. Frazer, Victoria Square, Adelaide, South Australia; John Theodore Hewitt, St. John's College, Cambridge; William James McKerrow, care of Hall, McKerrow, and Co., Nich las Street, Manchester; George Harry Major, Coldstream Street, Llanelly; Reginald Edensor Stanley Richardson, Elmfield, Knighton, Leicester; Thomas Shortridge Tweedie, The Moat, Annan; George Isaac James Wells, F.I.C., Kinderton Lodge, Middlewick, Cheshire.

The following were duly elected Fellows of the Society:—Arthur Adams; Frederick Edward Adams; Frederick Fielding Bond; William John Atkinson Butterfield; Hugh Brown Collins, B.Sc., C.E.; Francis V. Darbishire; Robert Brooke Floris; Alfred Thomas Gailleton; William Percy Hatton; James Hendrick; John C. Hewlett; Lionel Manfred Jones; Albert Henry Lockett; William Cossar Mackenzie; John Edward Whitley McFall; Charles Stephen Meacham; James Hill Millar; Robert Ludwig Mond; William Shields Myers; William Pullinger; Ernest John Parry; Charles Frederick Seymour Rothwell; Thomas John Buckler Sandercock; James Alexander Schofield; Thomas Skurray; George P. Darnell Smith; Henry John Spray; Alfred James Squires; James Sykes; Morris William Trewers; Hugh Woods.

The following papers were read:—

108. "A Search for a Cellulose-dissolving (Cytohydrolytic) Enzyme in the Digestive Tract of certain Grain-Feeding Animals." By HORACE T. BROWN, F.R.S.

The author, in a recent paper by himself and G. H. Morris (C. S. Trans., 1890, 459), has shown that during germination of the seeds of the grasses the cell-membrane of the endosperm is broken down and destroyed by a specific cellulose-dissolving enzyme, or *cytohydrolyst*; and that the breaking down of the cell-wall is a necessary preliminary to the dissolution of the reserve starch and proteids of the cell contents, which otherwise would not readily come under the influence of the extremely indiffusible starch and proteid-dissolving enzymes secreted by a certain layer of cells in the embryo.

As it was found by the author that the analogous starch-hydrolysing enzyme of animal saliva and of the pancreatic secretion experiences the same difficulty in traversing the thin cell membrane, it appeared almost certain that in grain-feeding animals there must be some provision in their economy for removing, during the processes of digestion, the inverting cell-membrane of the starch-containing cells of the interior of the grain, and of

thus bringing the cell contents fully under the influence of the digestive enzymes of the alimentary canal.

An examination of the contents of the small intestine of a pig, fed a few hours before death with barley-meal, conclusively showed that by the time the food had reached this point the originally intact parenchymatous cell walls of the grain had undergone almost complete dissolution, and that the starchy and proteid cell-contents had been completely freed from their cell envelopes and were being rapidly dissolved under the influence of the pancreatic secretion.

As the phenomena were in the highest degree suggestive of the cell wall being dissolved by an enzyme, the search for this cytohydrolyst was commenced by a very full examination of the *pancreas*, that of the *pig*, *horse*, *ox*, and *sheep* being employed, but not the slightest evidence could be obtained that this organ is capable of secreting an enzyme having any action on cellulose.

A continuance of the search in the small intestine itself, which is known to possess certain hydrolysing functions, was rendered unnecessary when it was discovered that the action on the cell wall of the grain food has already taken place before the stomach contents have passed into the small intestine. It was, therefore, in the stomach itself, or in the salivary glands, that the search had to be continued; but the enquiry was further narrowed by the fact that animal saliva was found to be incapable of exercising any action on cellulose.

The experiments on the stomach membrane and stomach contents were all made on the *horse* and the *pig*. The dissolution of the vegetable cell membrane in the stomach may be due to one or more of the following causes, viz.:—

1. To mechanical disintegration brought about by the "churning" and "propulsive" movements of the stomach during digestion.

2. To the action of the natural acids of the stomach, which may bring about the dissolution of the cellulose either (a) by direct hydrolysis, or (b) by converting a zymogen of the grain into an active cytohydrolyst.

3. To the action of a special enzyme secreted by some portion of the mucous membrane of the stomach.

4. To the direct or indirect action of living micro-organisms. These may break down the cell wall by:—

- (a). A direct attack of the living organism without the intervention of a secreted enzyme.

- (b). A previous secretion by the organism of a special cytohydrolyst.

- (c). An indirect production of a cytohydrolyst by the modification of some of the constituents of the grain by the vital processes of the micro-organisms.

5. To the self-digestion of the food under the influence of a cytohydrolyst pre-existent in the grain before ingestion.

Each one of these possible cases had to be examined separately in order to determine the *vera causa* for the destruction of the parenchymatous cell wall which undoubtedly takes place in the stomach during digestion. It is shown by numerous experiments that the destruction of the membrane is not due to mechanical disintegration nor yet to any action of the stomach acids, nor is it attributable to the direct or indirect influence of micro-organisms. The cell wall is, undoubtedly, dissolved by a cytohydrolytic enzyme; but, contrary to what was expected, this enzyme is not secreted by any portion of the mucous membrane of the stomach, but is pre-existent in the grain before ingestion, the animal itself contributing nothing to the result except by affording suitable conditions of temperature, &c., for the action of the enzyme.

In a previous paper by the author and G. H. Morris (*loc. cit.*) it was stated that the cellulose-dissolving enzyme which is of so much indirect importance to the plantlet during the germination of the seeds of the grasses is not pre-existent in the seed during its resting stage, but is a

product of the germinative processes. Although this is strictly true as regards the morphologically perfect and highly-matured barley which was used during the greater part of that research, it is not strictly true of all barley or grasses, especially of barley grown in this country under somewhat imperfect climatic conditions. This, as a rule, contains even in its resting state more or less of the cellulose-dissolving enzyme, and the same is true as regards *rye*. In *oats* the cytohydrolyst is particularly abundant, and this fact explains the very great rapidity with which the endosperm of the oat is disintegrated in the early stages of digestion in the horse as observed by the author, and also throws considerable light on the cause of the high estimation in which oats are held as a food-stuff.

That the dissolution of the cell membrane is due wholly and entirely to the cytohydrolyst of the food-stuff was proved by making a parallel series of experiments on animals fed in the one case with barley-meal which was destitute of cytohydrolysing power, and in the other case with the same meal to which a small amount of germinated grain had been previously added. In the first instance no destruction of the parenchymatous cell wall took place in the animal's stomach; whilst in the second case the vegetable membrane was completely dissolved in a very short time.

The presence of a cytohydrolyst and its amount in the food of grain-feeding animals is a factor, and, perhaps, a very important one, in their nutrition, for the more or less complete preliminary preparation of the food in the stomach before it passes into the intestine cannot be a matter of indifference to the animal physiologically.

The experiments have a very important bearing on the lengthy investigation carried out at Rothamsted, some years ago, on the relative value of malted and unmalted grain as a food for stock. The whole of the subject requires re-examination from a new point of view, and it does not seem at all unlikely that the supposed condimental value of malt, which has been insisted on by many agriculturists in the face of the Rothamsted experiments, may, after all, be a fact.

DISCUSSION.

Mr. BROWN, in reply to Professor Tilden, said that the enzyme in question was undoubtedly distinct from diastase and unable to attack starch. With reference to the question put by Professor Green, whether the cæcum of herbivora was not the seat of the digestion of the cellulose in the major portion of their food, he thought that it was clearly shown by Tappeiner's experiments that this was the case, and that its digestion was effected through the agency of micro-organisms. He was unable at present to give any reply to Mr. Cross's question as to the behaviour of the different varieties of cellulose.

109. "On the Influence of Oxygen and Concentration on Fermentation." By ADRIAN J. BROWN.

The author describes experiments on the reproductive power of yeast, from which it appears that all fermentable nutritive solutions encourage the increase in number of yeast cells, to some fixed point beyond which they will not reproduce themselves; and he shows that if a greater number of cells be introduced into a fermentable liquid than the liquid could originally develop, no increase in number of cells takes place. As under conditions like these fermentation still proceeds vigorously, a number of disturbing factors which complicate the results obtained under ordinary conditions may be eliminated by using non-multiplying yeast cells.

A series of experiments are described in which fermentations were conducted in presence of large amounts of oxygen, whilst at the same time duplicate experiments were made in which oxygen was excluded; the same number of non-multiplying yeast cells being used in both cases, and all the other conditions, such as temperature, agitation, &c., being kept constant. Under these circumstances it was found that both equal numbers of yeast cells and

equal weights in presence of oxygen exercised more fermentative power than when unexposed to its influence. The author is unable to reconcile these results with M. Pasteur's theory of fermentation.

Experiments carried out with a fixed number of non-increasing yeast cells also showed that the amount of sugar fermented in a given time by them did not depend on the concentration of the solution, but that within the limits of 20 and 5 per cent solutions of dextrose, approximately the same weight of sugar was fermented. When the strength of a solution reaches 30 per cent of dextrose fermentation proceeds much more slowly.

110. "Limettin." By WILLIAM A. TILDEN, D.Sc., F.R.S.

Limettin is the name given by the author to a crystalline substance deposited from the essential oil of the lime, originally described by him in conjunction with C. R. Beck (*C. S. Trans.*, 1890, 323).

Further investigation of its properties shows that, instead of the formula $C_{16}H_{14}O_6$ first attributed to it, limettin has the composition expressed by the molecular formula $C_{11}H_{10}O_4$, which requires nearly the same percentages of carbon and hydrogen.

By the action of nitric acid it is converted into a nitro-derivative $C_{11}H_9(NO_2)_4O_4$, and by the action of bromine into a dibromo-derivative $C_{11}H_8Br_2O_4$, while chlorine converts it into a trichloro-compound $C_{11}H_7Cl_3O_4$. The dibromo-compound also exchanges the third atom of hydrogen for chlorine, giving $C_{11}H_7BrClO_4$. Oxidising agents convert limettin into acetic or oxalic acid without definite intermediate products. Potash fusion produces from it phloroglucol and acetic, but no other acid. Treatment with concentrated solution of hydrogen iodide causes the elimination of two methyl groups.

Sulphuric acid slightly diluted causes limettin to assimilate a molecule of water forming a phenolic compound of which the diacetate was prepared and analysed.

Limettin is not attacked by acetyl chloride, by phenylhydrazine, or by sodium amalgam, and it gives no colouration with ferric chloride. It forms very pale yellow thin prisms, which melt at 147.5° ; it dissolves in alcohol, benzene, toluene, and acetic acid pretty freely, but scarcely in water or in light petroleum. Dilute solutions exhibit a beautiful violet fluorescence. It seems to have the constitution $C_6H_3(OCH_3)_2 \cdot C_3HO_2$. Further experiments are in progress.

111. "The Acid Action of Drawing Papers." By C. BEADLE.

Professor W. N. Hartley has recently communicated a note on this subject (*Proc. C. S.*, 1892, 19) which raises questions of considerable technical importance. The fact of the "acidity" of papers need not be discussed, and Professor Hartley's contention that an acid constituent in the paper has a serious effect on "water-colours" applied to the paper I am not in a position to criticise. I merely wish to point out that the author is probably in error as to the cause of the acidity, which he takes to be a residue of sulphuric acid left in the "fibré" (rags) after the process of "sourcing" and washing.

The mill where the "Whatman" papers are made is situated at Maidstone, and the water used in the manufacture is the characteristically hard water of that district. The "sourcing" of the rags is followed by a long process of continuous washing in the "engine," and after some years' experience of paper making in the Kentish district I am satisfied that no acid can survive this treatment.

On the other hand, the papers are sized with gelatin and alum, and it is to the presence of the latter constituent that the "acidity" is, in my opinion, due. In a recent examination of one of these papers I obtained, by treatment with distilled water, an exhaust which showed "acidity" equal to 2.3 c.c. normal H_2SO_4 per 100 grms. paper, using *litmus* as indicator in the titration, and yet this exhaust was basic to methyl orange. Sulphate of alumina, $Al_2(SO_4)_3$, being acid to methyl orange, the evidence is

complete that the apparent "acidity" of the aqueous exhaust is due to the presence of a basic sulphate of alumina (*cf. Jour. Soc. Chem. Ind., 1891, 202*).

OBITUARY.

THE LATE PROFESSOR DITTMAR.

By the death of Professor Dittmar, of Anderson's College (Glasgow and West of Scotland Technical College), the world of chemistry and physics has suffered a great loss. Since he first came among us some thirty-three years ago, at the invitation of Prof. Sir Henry Roscoe, who, meeting him and recognising his worth in the laboratory of the distinguished Bunsen, invited him to become his private assistant, Wm. Dittmar's name has steadily increased in repute as a worker in, and exponent of, his science. Dying, as he did, literally in harness,—for he left his lecture-room for his death-bed, and calmly summed up the events of his last day with the words, "Well this morning, ill to-night, dead to-morrow,"—even if he had been but a good average man, who did his duty so as to give fair satisfaction, some words of regret and praise would have been not ill-spent by the side of his suddenly opened grave. But the great variety of Prof. Dittmar's labours as a lecturer, analyst, chemical expert in legal cases, writer, investigator, and discoverer; his long enthusiastic devotion to science; his association as a collaborator with some of the most distinguished British chemists; his influence on the many promising young chemists trained after his methods; not to mention his striking individuality and sterling worth as a man, all call for a hearty tribute of admiration and respect to his memory and of sympathy with his family.

Born in Umstadt, near Darmstadt, in 1833, which latter town has been the birthplace of Liebig, Strecker, Kekulé, and Schorlemmer, Wm. Dittmar meant at first to follow the profession of a pharmacist, but eventually entered in 1857 the laboratory of Bunsen, who soon offered him an assistantship.

Sir Henry Roscoe having, as already mentioned, here asked him to assist him, took Mr. Dittmar with him to Manchester. In 1861 he became chief assistant to Sir Lyon Playfair, and in this way became the teacher of Prof. Dewar, whose respect and friendship for his old master has been all along warm and pronounced. Until 1869 he was well known to Edinburgh students as embodying the enthusiasm, abstraction, and untiring devotion to work understood to be characteristic of the typical German Professor, but all held him in honour for his high character, simple kindly nature, and marked abilities. It was to everybody's satisfaction that after three years in his native country spent in the work of "Privat Docent," at Poppelsdorf, where, we believe, he delivered a course of lectures on meteorology, he preferred to refuse a chair at Cassel, and to accept in 1872 his old post at Edinburgh under Prof. Crum-Brown, with whom there was thus renewed a deep friendship. About a year afterwards Mr. Dittmar was appointed to the newly-instituted Chair of Practical Chemistry in Owen's College, but returned to Scotland in 1873 to occupy that of Chemistry in the Andersonian University of Glasgow. Every one knows that this Chair has been long remarkable, rather for the celebrity of its occupants than the worth of its emoluments.

Prof. Dittmar found in the Anderson's College a sphere not uncongenial to him. The day was past when one might hope to reimburse himself for his efforts so well as the popular and brilliant Penny did, but Dittmar set himself steadfastly to sustain the tradition of fame which Graham's genius had gained, and Ure's great repute as an industrial chemist had maintained in Anderson's

College. He felt, moreover, and acknowledged the competence of Thorpe whom he succeeded. How successfully he upheld the repute of his Chair his wide popularity as a lecturer has attested. The laboratory-roll from small beginnings rose to sixty-three, and has for years averaged fifty; an increase which, be it observed, scarcely anyone will be disposed to deny arose from Prof. Dittmar's great personal reputation as a laboratory trainer. The men who have been thus trained are at one in viewing his influence and power as a teacher as quite extraordinary, —an estimate which may take its complexion from daily contact with a nature so kindly and cheerful, a critical power so genially trenchant, and knowledge and fertility of resource so vast as those of Prof. Dittmar, but which is substantiated by a perusal of the various manuals of instruction that bear his name.

It is not out of place to mention shortly the chief publications in which Prof. Dittmar has made known his views and the results of his research.

His contributions to chemical literature have been very numerous as well as voluminous, and anyone who has read them will be struck with the freshness of illustration, the mastery of detail, the clearness of statement, and the well balanced method with which they are written. In proof of this we may single out the article "Analysis," in the Second Edition of "Watts's Dictionary of Chemistry"; the article on "Fermentation" in the "Encyclopædia Britannica," New Edition, and a masterly article of marked individuality on the "Atomic Theory" in the "National Cyclopædia." The substance of this last, if we mistake not, was originally part of a projected but only partly completed work on organic chemistry, and it lies alongside of a contribution to the Royal Society of Edinburgh (1878), in which he expresses his belief that the true way to demonstrate Dalton's law of multiple proportions is to represent it as a necessary corollary of the assumption of the atomic theory with Avogadro's supplement.

To the "Encyclopædia Britannica," New Edition, Prof. Dittmar contributed also the important articles on metals and metallurgy, the potassium metals, the platinum metals, besides briefer ones on silver, nickel, mercury, manganese, magnesium, tin, titanium, lanthanum, tungsten, molybdenum, lime, sulphur, selenium, silicon, &c.

Besides occasional articles of an industrial character, such as those on "Alkali Proof Vessels" and "Tension Thermometers and Pyrometers," in the *Jour. Soc. Chem. Ind.* (1884 and 1885), he contributed regularly to the *Chemische Industrie*. Before the Royal Society of Edinburgh he laid at least three extensive researches:—

1. Dittmar and Fawsitt, May, 1887, "Contribution to our Knowledge of the Physical Properties of Methyl Alcohol."

2. Dittmar and MacArthur, July, 1887, "Critical Experiments on the Chloroplatinate Method for the Determination of Potassium, Rubidium, and Ammonium; and a Re-determination of the Atomic Weight of Platinum." At the close of this very satisfactory research he fixes this last as not far from 195.5, and holds that to agree well with Seubert's result.

3. June, 1889, "On the Behaviour of the Hydrates and Carbonates of the Alkali Metals, and of Barium at High Temperatures; and on the Properties of Lithia and the Atomic Weight of Lithium."

In 1884 was published Prof. Dittmar's report "On the Composition of Ocean Water," which formed part of the treasure given to science by the famous *Challenger* Expedition of 1873—1876. To the seventy-seven waters, of which the report furnishes a complete analysis, he did the utmost justice. The task, as he carried it out, was colossal, but not more so than his patience and indefatigability. It seemed, as the critic in *Nature* puts it, "more like a life-work than that of six years." How largely and ably both mathematics and physics were laid under contribution to obviate probable error,—with how much foresight, caution, and ingenuity the work was

carried on, can only be quite understood by a careful consideration of the full report, but some idea may be got by reading the digest in which Prof. Dittmar summarises his *Challenger* work for the benefit of the Philosophical Society of Glasgow (December, 1884).

He concludes that free CO_2 in ocean water is exceptional; that in surface waters, as the temperature falls, the proportion of CO_2 increases, and *vice versa*; and that within equal ranges of temperature the proportion of CO_2 is lower in the surface waters of the Pacific than in those of the Atlantic.

Setting out in the track Forchhammer pursued in 1864 Dittmar outstripped him, and is to be regarded as our final authority for considering that while the salinity of the ocean is variable, the relative proportions of the salts are practically balanced. But upon these results Prof. Dittmar did not plume himself, saying expressly that "whatever may be the merits of his work, its better part consists of critical investigations into old, and attempts at inventing new, analytical processes." Notwithstanding the diffidence with which Prof. Dittmar regarded the value of his work in respect to oceanography, it is universally esteemed to be the greatest published contribution to the chemistry of ocean-water, and, as such, is a public as well as a scientific service of the highest merit. Pre-eminently fitted by his nature, experience, genius, and opportunities to test by re-trial and modification the results of earlier great workers, Prof. Dittmar, with the co-operation of Mr. J. B. Henderson, undertook an investigation of the "Gravimetric Composition of Water," given to the Philosophical Society of Glasgow, December, 1890. This, as all know, to be worth anything, entailed work of the severest kind, and could only be a labour of pure love for chemical science.

It is impossible, without reading the detailed account of the research, to grasp the closeness of the criticism applied to Dumas' work, or the ingenuity with which its defects are accounted for and remedied. Dumas' neglect of "vacuum corrections," Erdmann's and Marchand's misplaced trust in the perfect drying power of fused chloride of calcium, Dumas' method-error, owing to atmospheric air in his hydrogen, the suspected and proved production of water by the action of hydrogen on hot glass, and the unexpected discovery that, even in the cold, hydrogen acts on oil of vitriol so as to give sulphurous acid; these and, indeed, the whole of the details, are not merely deeply interesting, but present to all who aim at research a lesson of the highest kind. It would have been strange indeed had not such a labour been in part repaid with the Graham Medal.

In all these investigations, whether undertaken for fee or for love's sake, the outstanding characteristics of Prof. Dittmar were such as did him honour not merely as a scientist but as a man. He was not merely a close reasoner, a happy adapter, a severe critic of himself as well as of others, a man of immense fertility and resource, willing to "toil terribly for truth's sake," but he showed in the self-estimate of his work great modesty and candour; in regard to the honest and ably done work of others a due respect, even when their results are opposed to his own; and a scrupulous care in acknowledging the aid and services of all his coadjutors.

"Being," says he at the close of his last research, "an incorrigible 'Proutian,' I do not give up the hope that the true number may be 1 after all;" and though he finds his result 1.0085 in the good company of Stas, Cook and Richards, Noyes and Rayleigh, he says "these five investigations might be said to settle the question were it not for Keiser, who finds 1.0032, and it is impossible to pass over his research!"

Besides being, as a theorist, the first to correctly interpret the dissociation of a solid substance and the author of the line of researches we have noticed, his memory has claims upon the respect of all laboratory workers as a high authority on precision-balances, a subject which he treats in "Thorpe's Dictionary" and elsewhere. His

"microscale" and "auxiliary gravity-bob," as made by Oertling and Staudinger, have been of great value in saving time and ensuring accuracy in weighing; and besides many improvements in processes and apparatus, his "differential method" of determining specific gravities of liquids is the most perfect known.

Professor Dittmar gave years ago to the world several works of a more purely academic character: a "Manual of Qualitative Chemical Analysis," of great erudition; an elementary book on "Analytical (Qual.) Chemistry;" and "Tables to Facilitate Chemical Calculations." More lately he published a book on "Quantitative Chemical Analysis," which, replete with fresh, well-chosen, well-arranged material, and thoroughly abreast of the latest improvements in processes, contains what has been hailed in all quarters as a most admirable exposition of the principles and practice of gas analysis. This work, and the unique and in great degree original first part of the "Chemical Arithmetic," more lately published, stand evidence of Dittmar's greatness as a teacher.

All who read his books, all who worked under his guidance, all who listened to his lectures, felt convinced that in him there was no mere compiler, no retailer of second-hand thought, but a mind of rare scientific attainment and insight unrelentingly at work. "Brain sucking"—to use his own strong expression—he despised, as likewise the degrading of great intellectual powers to mere money-making. Genial, simple, lovable, he was the staunchest of friends, and the most resolute of opponents. He could only view things from what he thought the stand-point of right—never from that of expediency.

He remained unspoiled by the honours which came to him in later years, and his dislike to parade himself at conferences may probably explain why so few of his chemical *confrères* know intimately the manner of man he was. We may fittingly apply to himself the words he utters in a short but admirable sketch of the great Wöhler and his work: "One student might wish to work on organic chemistry, another on minerals, a third on metallurgy, a fourth on rare elements; let them all go to Dittmar, and they all, like the fifth or sixth, would find themselves in the right place!" Equally appropriate to himself is the well-pleased reflection with which he closes the sketch: "He continued working to almost the edge of his grave."

CORRESPONDENCE.

THE DIRECT COMBINATION OF CHLORINE WITH METALS.

To the Editor of the Chemical News.

SIR,—In the last number of the CHEMICAL NEWS (p. 101) is an article with the above heading by U. Kreusler. The author would appear to be somewhat surprised that dry chlorine had no action on brass wire.

Twenty-eight years since I patented a process for purifying bone-black, in which it was shown that, while dry chlorine gas or dry hydrochloric acid gas would combine with the dry carbonate of lime deposited in the bone-black during the sugar refining process, it had no action whatever on a much more soluble substance than brass, viz., the dry tribasic phosphate of lime of the bone-black.—I am, &c.,

EDWARD BEANES.

Moatlands, Paddock Wood,
Feb. 29, 1892.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

SIR,—The reply inserted in your last issue (p. 106) to the letter of your correspondent "W. S." will, I think, be a

very disappointing one to the Society of Students. It is all very well for "C. O. O." to say, "Seek first the Science and its discipline and all those things shall be added." It seems to me that "C. O. O." has not thoroughly grasped the idea intended to be put forward by "W. S." Chemistry is such an extensive science that one cannot hope, even with the hardest study, to excel in every branch of it. Very few men thoroughly qualified for the position of chemist in a works are competent to teach a class of students who, in their turn, intend to become teachers of the pure science.

Between the branches of chemistry (as divided by Mr. F. Woodland Toms, in his letter at p. 105), viz., the analytical chemists in works, the analyst pure and simple, and the professor who is open for consultation there is a wide difference, and the point to be discussed is which of the branches is likely to be most beneficial to a student.—I am, &c.,

F. G. M.

Manchester, Feb. 29, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 7, February 15, 1892.

A New Method of Organic Analysis.—M. Berthelot.—The method consists in burning the substance under examination in the calorimetric bomb in oxygen compressed to 25 atmospheres. The combustion is complete and instantaneous, contrary to what takes place in combustions by copper oxide. When the combustion is effected the gases are allowed to escape from the bomb through the ordinary system of tubes for organic analysis, a desiccating tube filled with sulphuric pumice, and then tubes with liquid and solid potassa. When this is effected the surplus gases are extracted from the bomb by means of a mercurial pump and caused to pass into the same absorbent apparatus. Purified air is then passed into the exhausted bomb, repeating the operation three or four times so as entirely to extract the carbonic acid. The determination of the carbon may be thus executed with great precision and promptitude. The determination of the hydrogen is rather more complicated. It may be effected by using dry oxygen and by slightly heating the bomb after the operation so as to evaporate all the water in the successive gaseous atmospheres which result from the foregoing operations. But we must take into consideration the traces of nitric acid produced during the combustion and volatilised at the same time as the water. The separate determination of the carbonic acid is not subject to this complication, as the water condensed in the bomb retains entirely these traces of nitric acid. The combustion in the bomb enables us also to determine completely the sulphur of organic matter by adding beforehand 10 c.c. of water; the sulphur remains in the water in the form of sulphuric acid, as we have demonstrated by very precise determinations. This is the most expeditious method for the determination of sulphur and also of phosphorus in organic compounds.

Use of Compressed Oxygen in the Calorimetric Bomb.—M. Berthelot.—Compressed oxygen may be introduced into the bomb in two different manners. It may be drawn from a gas-holder filled beforehand at the ordinary pressure, saturated with moisture, and then compressed in the calorimetric bomb. In this case the entire space is necessarily saturated, and a certain quantity of watery vapour is condensed capable of restoring the saturation at the end of the experiment. As the final tem-

perature is higher than the initial temperature by about 3°, it results that a small quantity of water has been evaporated during the experiment. But this quantity is so small that it does not introduce an appreciable correction. It is different if we make use of a receiver filled with oxygen compressed beforehand at a pressure of 100 to 120 atmospheres. Such oxygen is dry or nearly so, and we have in most combustions to take into account the evaporation of the water in the void space of the bomb. This quantity may be neglected in industrial operations but not in strict scientific researches.

Action of the Alkaline Metals upon Boric Acid. Critical Study of the Processes for the Preparation of Amorphous Boron.—Henri Moissan.—The author has examined the boron of Gay-Lussac and Thenard, that of Deville and Woehler, and that of Berzelius, none of which are pure. If we cause an alkaline metal to react upon boric acid the reaction takes place with a great liberation of heat, by means of which the greater part of the boron which had been set free combines with the excess of the alkaline metal, and with the metal from the apparatus in which the reaction has been effected. If we afterwards exhaust the product with water and hydrochloric acid we obtain, after desiccation, a mixture of boron, sodium, and iron borides, boron hydride and nitride, and hydrated boric acid. This is the mixture which has hitherto been regarded as amorphous boron.

Light of a Temporary Star in Auriga.—G. Rayet.—The spectrum of this star consists of a continuous spectrum in which the red and the violet appear very luminous, and of four brilliant bands in the green, the wave-lengths of which are:—No. 1, 518 μ , near *b*; No. 2, 501; No. 3, 493; No. 4, 487, near *F*, very probably *F*. The most brilliant of these bands are the second and the third. A more recent observation in the night between February 14 and 15 enabled the author to detect the brilliant line *H α* of hydrogen in the red and that of sodium.

Determination of the State of Dissolved Salts according to a Study of their Contraction.—Georges Charpy.—This paper requires the two accompanying diagrams.

On Certain Properties of Bismuthic Acid.—G. André.—If after obtaining bismuthic acid as pure as possible we try to re-combine it with potassa, it is impossible to obtain the neutral salt BiO_3K . The author has previously shown how bismuthic acid is commonly obtained by passing a current of chlorine into a hot concentrated solution of potassa holding bismuth oxide in suspension. In the preparation of bismuthic acid effected either with a bromised solution of bismuth bromide in presence of potassa, or by means of chlorine acting upon the oxide in presence of potassa, a persistent emulsion is produced by prolonged washing. We remark the tendency of bismuthic acid to produce complex bodies by uniting with its own anhydride. Are such compounds truly definite?

On a Definite Barium Carbide.—M. Maquenne.—Barium carbide corresponds to the formula C_2Ba . Its decomposition by water may be expressed by the following equation, $\text{C}_2\text{Ba} + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{Ba}(\text{OH})_2$. It is evident that barium acetylide, like the nitride, must play an important part in the synthetic production of the corresponding cyanide.

On the Principles which Accompany Chlorophyll in Leaves.—A. Etard.—The author demonstrates in presence of chlorophyll the existence of a triatomic alcohol, *oenocarpol*, a diatomic alcohol, *vitoglycol*, and a monatomic alcohol, *medicagol*. These new crystalline compounds resemble cholestérine only in their outward appearance.

Transformation of the Aromatic Amines into Chlorohydrocarbides.—M. Prudhomme and C. Rabaut.—The chromic, ferric, &c., chlorides, act like cupric chloride upon diazobenzene chloride. For the reduction

of the nitrates of the aromatic amines, and their transformation into chlorohydrocarbides, we may substitute for cuprous chloride the chromous chloride, which is also a very energetic reducer. The ferrous and stannous chlorides do not determine the reduction of nitrates and transformation into diazo-derivatives.

On the Assimilation of the Carbohydrates.—M. Hanriot.—Glucose introduced into the animal organism does not undergo simply a combustion or a transformation into glycogene, but it is converted quantitatively into fat.

Journal für Praktische Chemie.

New Series, Vol. xlv., Parts 18, 19, and 20.

Oxidation of Mixed Monocarbonyl Ketones of the Aliphatic Series.—G. Wagner.—The oxidation of the mixed ketones, in which the two atoms of carbon adjacent to the carbonyl are hydrogenised, takes place at 100° generally in two directions, chiefly in that in which the most heat is liberated.

Oxidation of Tertiary Alcohols.—G. Wagner.—The oxidation of the tertiary alcohols consists probably in the hydroxylation of one of the atoms of carbon directly combined with the group C(OH), whereby the oxidation of such tertiary alcohols in which these carbon atoms are hydrogenised to a different extent and combined with different radicals, probably by the same or similar rules which we have encountered in the ketones.

Researches from the Laboratory of the University of Freiburg.—These consist of the 45th memoir by Ad. Claus on the oximes and the so-called stereo-chemistry. The author contends that these and all the phenomena of isomerism which are known for the production of the transposition of benzil and hydroxylamine may find a simple explanation, as depending upon structural isomerism without the help of any stereo-chemical hypothesis.

Calorimetric Researches by F. Stohmann. 25th Treatise: On the Thermic Value of the Constituents of Nutriments and their Derivatives.—F. Stohmann and H. Langbein.—This voluminous essay with its many tables does not admit of useful abridgment.

Remarks on the Paper by Ad. Claus: "The Transposition of Bibromsuccinic Ester with Zinc."—Arthur Michael.—This discussion is becoming very warm, and A. Michael declares that, as far as he is concerned, it must cease.

Communications from the Chemical Institute of the University of Kiel. No. 11.—These consist of a paper by A. Heuser and C. Stoeck, on methylated dipyrilids.

The Bismuth Controversy.—A. Classen replies to the paper of H. R. Schneider (*Journ. f. Prakt. Chemie*, vol. xlv., p. 23). He shows that the bismuth used by Schneider for determining its atomic weight was by no means pure.

On the Translocations of the Propyl Group.—Oscar Widman.—The author does not believe that any doubt exists as regards the translocations within the propyl group of the cymol and cumic derivatives.

Some Thio-derivatives of Orthoaminobenzamide.—Andrew Stewart.—A preliminary communication.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xvi., No. 2.

New Mechanical Process for the Continuous Manufacture of Agglomerated Soaps compared with the Present Process.—Jos. Goffin.—The improvements described in this paper are purely mechanical.

Purification of Cupriferoous Bismuth.—Ed. Matthey.—From the CHEMICAL NEWS.

MEETINGS FOR THE WEEK.

- MONDAY, 7th.—Medical, 8.30. (General Meeting).
— Royal Institution, 5. General Monthly Meeting.
— Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).
- TUESDAY, 8th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Medical, 8.30. (Annual Dinner).
— Photographic, 8.
- WEDNESDAY, 9th.—Society of Arts, 8. "Experiments on the Durability of Modern Pigments," by A. P. Laurie, M.A.
— Geological, 8.
— Pharmaceutical, 8.
- THURSDAY, 10th.—Royal, 4.30.
— Institute of Electrical Engineers, 8.
— Mathematical, 8.
— Royal Institution, 3. "The Progress of Romance in the Middle Ages," by Prof. W. P. Ker, M.A.
- FRIDAY, 11th.—Royal Institution, 9. "Japanesque," by F. T. Pigott.
— Astronomical, 8.
— Physical, 5. "Thermodynamics and the Action of Light on Silver," by Mr. H. M. Elder. "On Choking Coils," by Prof. J. Perry, F.R.S.
- SATURDAY, 12th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

ERRATUM.—P. 102, col. 1, line 17, for "1-200th" read "1-2000th."

ENGLISH TRANSLATION OF MENDELEEF'S CHEMISTRY.

The Principles of Chemistry.

By D. MENDELEEF,

Professor of Chemistry in the University of St. Petersburg.

TRANSLATED BY

GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg,

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A. J. GREENAWAY, F.I.C., Sub-Editor of the Journal of the Chemical Society.

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THE CHEMICAL NEWS.

Vol. LXV., No. 1685.

PRELIMINARY NOTE ON NOVA AURIGÆ.*

By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S., and
Mrs. HUGGINS.

We have delayed up to the present time presenting any account of our observations of Nova Aurigæ, in the constant hope that fine weather would enable us to make our observations more complete. We think now, however, that it may be of interest without further delay to send a short preliminary notice of this remarkable, and, in some respects, unprecedented, celestial phenomenon. For up to this time we have no record of a star in the spectrum of which the bright and dark lines of the same substances have been regarded as indicating respectively motions of approach and of recession of so great magnitude. It was partly for this reason that we were anxious for the opportunity of observing if any change in the amount of relative motion would show itself.

We received a telegram from Dr. Copeland in the early morning of the 2nd inst., and began our observations of the star on the night of the 2nd inst.

Perhaps the most noticeable feature to the eye in the star's spectrum was the great brilliancy of the hydrogen lines at C, F, and G; but the point of greatest interest was obviously that two of these lines, F and G, and we have since observed the same with C, were accompanied each by a strong absorption line on the side towards the blue. Comparison with the lines of terrestrial hydrogen, while confirming the obvious presumption that the star lines were really those of hydrogen, showed at once a large motion of recession of the bright lines and a motion of approach of a similar order of magnitude of the hydrogen which produced the absorption.

A photograph which we have since taken gives the star's spectrum as far in the ultra-violet as about λ 3200. On this plate we see not only the other hydrogen lines at h and H, but also the series beyond, which is characteristic of the white stars, bright, with dark absorption lines on the blue side.

Besides the hydrogen series, there appear to be other lines doubled in similar manner, including the sodium line at D. The line K is strongly impressed upon the plate, but in our photograph is not followed by an absorption so strong as in the case of H, where the absorption may be two to substances.

In the green part of the spectrum three very brilliant lines are seen on the red side of F. One of these falls not far from the position of the chief nebular line; but even when the shift of the spectrum is taken into account, we can scarcely regard this line as the true nebular line. In this connection it was a point of some importance to find that the strong and very characteristic line of the Orion nebula, which falls about λ 3725, is absent in our photograph of the nova, also the strong nebular line between α, β at about λ 3868. The third line from F is rather broad and resolvable into lines. It falls partly upon the more refrangible pair of the magnesium triplet at b , but its character and position do not permit us to ascribe it either to magnesium or to carbon.

We wish to mention an early photograph of this star taken on the 3rd inst., by Father Sidgreaves, at Stonyhurst, which we had the privilege of examining. This successful photograph extends from about h to near D, and shows the remarkable doubling of many of the bright lines by dark ones, a feature which was at once noticed by Father Sidgreaves and ourselves.

In our photograph, the spectrum of the star, which extends on the plate as far into the ultra-violet as our photographs of Sirius, is crowded throughout its entire length with dark and bright lines. In the visible region the number of bright lines and groups, including the double line of sodium, a fine line about the position of $\frac{D}{3}$, and lines on both sides of C, is also very great.

We prefer in this preliminary note not to enter into any more detailed discussion of the star's spectrum, nor to refer to the probable phenomena which may now be in progress in this celestial body. We reserve these considerations for the present.

PROFESSOR BUNSEN AND THE CHEMICAL SOCIETY.

It was announced at the last meeting of the Chemical Society that it was proposed to present the following address to Professor Bunsen, who has now been fifty years a Foreign Member of the Society, and the wish was expressed that among those who sign it all those who have been his pupils should, as far as possible, be included. Fellows of the Society who have been pupils of Professor Bunsen are requested to communicate with the Senior Secretary before March 19, in order that they may receive a form for signature.

*To Privy Councillor Professor Bunsen, Fellow of the
Royal Society.*

YOUR EXCELLENCY,

Fifty years have elapsed since the Chemical Society of London honoured itself by electing you one of its Foreign Members. Your name, and that of your illustrious fellow-countryman Liebig, are, in fact, the first on a list which includes the most distinguished cultivators of chemical science in every civilised country of the world.

Our Society remembers with gratitude that you enriched the first volume of its Transactions by communicating to it the results of your ever-memorable investigation of Cacodyl and its Compounds. That you should have sent to us, in the first and most critical year of our existence, a memoir which the chemical world will ever regard as one of the classics of our science, is a significant proof of the beneficent interest with which you regarded our efforts to foster the growth of chemical learning in this country.

Your masterly investigations, in collaboration with our Fellow Sir Lyon Playfair, on the gases evolved from iron furnaces, made by methods which you were the first to bring to perfection, greatly extended our knowledge of the theory of the smelting of iron. By the permanent benefit thus conferred on one of the most important of our industries, you have largely augmented our national wealth.

The half century during which you have been associated with our Society has been fruitful in great discoveries and important inventions. It has witnessed the birth of new elements, the creation of new analytical methods, and an extraordinary development in the instrumental resources of our laboratories. Chemists will never forget that it is to your unwearied assiduity and single-minded devotion that science owes some of the most momentous of these discoveries, and some of the most valuable of these inventions. Your investigations will ever be regarded as models of the highest type of scientific research, and the memoirs in which you have embodied them shed an imperishable lustre on our literature. Your methods of analysis are among the most common of our manipulative operations, and the very furniture and instruments of our laboratories are an ever-present testimony to the obligations under which experimental chemistry will always remain to you.

* A Paper presented to the Royal Society, February 24, 1892

Many of our members are proud to be numbered among your pupils, and those among them who have become teachers have, we trust, caught and transmitted something, not only of the method, but also of the spirit, in which they themselves were taught. They have an abiding memory of your kindness, of your constant and unselfish devotion to their interests, and of the generous sympathy and ready help which you extended to their efforts to enlarge the boundaries of our science.

We, the undersigned Fellows of the Chemical Society of London, now beg to offer you our heartfelt felicitations on the occasion of your Jubilee as a member of our body. It is our fervent hope that you may be able, for many years to come, to enjoy the health and happiness the leisure and repose which you have so justly and so honourably earned.

NOTE ON THE MIGRATION OF SALTS.

By Dr. T. L. PHIPSON, F.C.S.,

Graduate of the Faculties of Science and Medicine of the University of Brussels, Member of the Chemical Society of Paris, &c.

DURING the many years that I have devoted to laboratory work, numerous more or less curious instances of the migration of salts have come under my notice. One of the most curious, and at the same time the most beautiful, was obtained by the spontaneous evaporation of a solution of *sulphonaphthalate of ammonia* placed in a very large glass capsule. The crystals formed along the sides of the capsule *over the mother-liquid*, producing the most exquisite representation of a coppice on the borders of a lake. For some weeks it was a cause of admiration and wonder to all who saw it.

But a still more extraordinary case of migration occurred a few years ago, which I will now describe. In 1883, when I published in the *CHEM. NEWS* a note on the "Constant Production of Oxygen Gas by means of the *Protococcus Pluvialis*," I had a small bottle of pure caustic soda used in analysing the air during these experiments. One morning the stopper was found to be tightly fixed in this bottle, and on striking it rather too impetuously with a knife, I produced three fine cracks, the stopper remaining as firmly fixed as before. The bottle was then put aside on a shelf, and not touched again till five years later. In 1888 it was found that almost the whole of the caustic soda had made its way out of the bottle through these three fine cracks in the upper part of the glass, and appeared on the outside in the form of a bulky covering of effloresced carbonate of soda, a large portion of which had fallen upon the shelf.

In the inside of the bottle are small quantities of minute, moist, quadrangular crystals. It is evident that the hydrate of soda has crawled up under the influence of the moisture of the atmosphere sucked in through the cracks, and has migrated through them to the outside, where, meeting with an ample supply of carbonic acid, it has been converted into carbonate, and this has subsequently effloresced, forming a bulky white covering like snow, a portion of which has fallen around.

In apparent defiance of the laws of gravitation, the contents of this bottle, which has remained in a perfectly quiescent state for five years, have found their way outside through these fine cracks which, occur only in the upper portion of it. It is doubtless a case of *capillarity*, and it may be stated, I think, as a general law that all cases of migration must be looked upon as phenomena of capillarity, although the exact nature of these phenomena seems still to be enveloped in mystery. Instead, however, of looking upon them as exceptions to the laws of gravitation, they must be connected with atmospheric pressure, and so come under their influence.

Laboratory of Analytical Chemistry,
Putney, London, S.W.

A GENERAL LAW APPLICABLE TO GASES AND LIQUIDS.

By J. ALFRED WANKLYN.

ONE of the results flowing from the work upon which I have been engaged for many years, sometimes alone and sometimes in company with my colleagues Cooper and Johnstone, is the unfolding of a great generalisation, applicable alike to gases and liquids, which may be formulated in the following terms:—

Heterogeneity is without influence upon volume, or the volume of a mixture is equal to the sum of the volumes of its constituents separately measured.

Gases.—So far as I am aware—although the reasoning on the simplest examples of gas-analysis involves the admission of the truth of this generalisation as applied to gases—the generalisation has never been explicitly set out. It is not by any means manifest *a priori*, but is founded upon very wide observation.

Thirty-one years ago it fell to my lot to place on record in the *Trans.* of the Royal Society of Edinburgh, a series of observations illustrative of the great truth that gaseous mixtures occupy exactly the same volume as the constituents of the mixture.

The paper has been frequently quoted, because in that paper Sir Lyon Playfair and myself announced the discovery of the duplicate nature of nitric peroxide, which is N_2O_4 at low temperatures and NO_2 at high temperatures. The completeness and the striking character of the evidence bearing upon the fundamental nature of gaseous mixtures has, however, escaped attention altogether, and it will not be out of place to refer to it in a detailed manner. The paper bore the title "On a Mode of Taking the Density of Vapour of Volatile Liquids at Temperatures below the Boiling-Point," by Dr. Lyon Playfair, C.B., F.R.S., and J. A. Wanklyn, F.R.S.E., and it was read January 7, 1861.

The method consisted in measuring the volume occupied by a mixture of a measured quantity of a permanent gas and an ascertained weight of the vapour under investigation; and our paper contained a detailed proof that such mixtures have the same volume as the sum of their constituent volumes, measured separately. We proved this for mixtures of alcohol and hydrogen, for mixtures of ether and hydrogen, for mixtures of nitrate of ethyl and nitrogen, for mixtures of nitric acid and air, and lastly, for the extreme case of a mixture of gaseous ammonia and gaseous water.

This last case I consider to be most important and most decisive. The details are, "a quantity of dry ammonia was measured over mercury, then a small portion of water, which had been accurately weighed in a thin glass bulb, was introduced into the ammonia. The whole was then heated up to $100^\circ C.$, and the volume of mixed gas and aqueous vapour noted.

	Observed c.c.	T. °	P. m.m.	Corrected vol. at 0.6 and 760 m.m.
NH_3	39.19	12.5	558.08	24.008
$NH_3 + H_2O$..	107.32	102	709.66	72.973

The weight of water employed was 0.0402 gm. On calculation it will be found that 0.0402 gm. H_2O yields 49.95 c.c. at 0.6 and 760 m.m., whilst the experiment gave 48.965 c.c., which, bearing in mind the experimental difficulties of such an experiment, is a sufficiently close agreement. In short, there is the most varied evidence that, so long as there is no actual chemical action between the molecules by a gaseous mixture, the fact of the molecules being dissimilar has no influence upon the volume."

Liquids.—The law holds in the instance of liquids just as in the instance of gases. Such, I believe, is the fair interpretation of the results which have been recently published in the *CHEMICAL NEWS* and in the *Philosophical Magazine*.

The basic numbers are 7-9; 7+9=16; 40=7+9=56; 39+39=78; and 39+39+16=94. And the anomalous group 12+12=24; 7+9+7=23.

ON SOME NEW PRODUCTS FROM INDIGO-BLUE.*

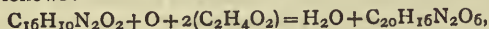
By CHARLES O'NEILL.

WHEN a very pure quality of indigo blue (such as is obtained by precipitation from an indigo vat) is treated in a mortar with twenty or thirty times its weight of mono-hydrated or glacial acetic acid, and permanganate of potash crystals added at intervals with constant stirring and grinding, the blue loses colour, the mass thickens, and upon being examined by a pretty high power of the microscope is found to consist wholly of small prismatic crystals floating in a nearly colourless liquid. Being collected on a filter, washed, and dried in a vacuum, or in air at a temperature of 20°-25° C., the new substance shows as a greyish, greenish, or bluish mass partially matted by the interlacing of the crystals.

Other oxidising matters effect the same change; such are dioxide of lead, red lead,—either added in powder or previously dissolved in glacial acetic acid,—and also the higher oxides of manganese.

The new substance is, no doubt, of a very pale yellow colour, the blue or green tinge being due to a small amount of indigo-blue enclosed in the crystals, which cannot be removed without danger of affecting the integrity of the body itself. The amount of permanganate required is about one-fourth of the weight of the indigo-blue, and equal to yielding one atom of oxygen to one molecule of indigo-blue; a corresponding amount of the other oxidising agents is found sufficient.

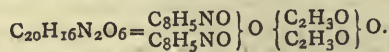
The equation representing the change may be expressed as follows:—



that is, indigo-blue plus oxygen plus acetic acid yield this body. The constitution of the body not being known it may be provisionally called *oxy-aceto-indigotin*. The calculated yield is about 145 for 100 of indigo-blue; up to 140 per cent has been obtained.

The oxy-aceto-indigotin is insoluble in all solvents which have been tried upon it, it is permanent in dry air, resists decomposition by most neutral, acid, and oxidising agents in the cold, is easily acted upon by alkalies, and is decomposed by heat in any menstrua.

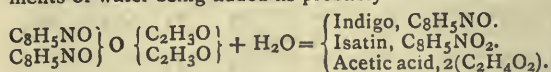
The decompositions of this new body are numerous, and some very complex; attention is for the present directed to only a few cases which are tolerably simple and easily followed. To trace these decompositions the following structure is assumed for the oxy-aceto-indigotin:—



It is not pretended that this is a true or even a rational arrangement, but it serves as a working hypothesis to explain some changes which the body undergoes.

Decomposition by Heat in Presence of Moisture.

When the oxy-aceto-indigotin is exposed to steam in a shallow vessel or boiled sufficiently long with water, it splits up into indigo-blue, isatin, and acetic acid, the elements of water being added as probably—



The calculated yield is acetic acid 31.6 per cent, isatin 34.5 per cent, and indigo-blue 38.7 per cent, which

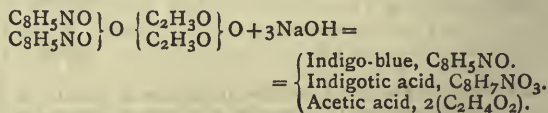
quantities have been frequently obtained. There is, however, usually a fourth body found in variable amounts from 1 per cent to 10 per cent which is less soluble in water than isatin, is dissolved by carbon disulphide in which isatin is insoluble, and crystallises from chloroform in silky golden-yellow crystals. It is believed to be formed by the interaction of indigo and isatin at the moment of their formation (*in statu nascendi*), and to be an oxidised product intermediate between these two bodies. A similar substance is produced under certain conditions by the direct oxidation of indigo-blue.

Decomposition by Dry Heat.

It requires a temperature of about 180° C. to completely decompose the oxy-aceto-indigotin, it loses 31-32 per cent in weight, and yields as distillate mono-hydrated acetic acid readily crystallisable; the residuum in the retort consists of indigo-blue and a red resinous matter which is best dissolved from the indigo by chloroform, leaving pure indigo; no isatin is produced.

Decomposition with Sodium Hydrate.

If the oxy-aceto-indigotin be mixed with solution of sodium hydrate in the cold, it speedily becomes blue-coloured, and in the course of some time may be filtered; indigo-blue is left on the filter, and a slightly yellowish filtrate is obtained; upon the addition of a mineral acid to the filtrate a precipitate is produced which, when separated, proves to be a new acid body which may, perhaps, properly be called *indigotic acid*. Using the scheme of construction given above, the decomposition may be assumed as follows:—

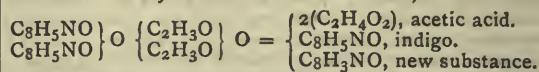


The Na of the sodium hydrate is replaced in this equation by H for sake of clearness and simplicity. The hypothetical acid $\text{C}_8\text{H}_7\text{NO}_3$ would be truly isatic acid, or isatin with the elements of water added; but upon combining the acid with bases it is found that the above formula must be quadrupled and stands $\text{C}_{32}\text{H}_{28}\text{N}_4\text{O}_{12}$.

This indigotic acid is yellowish or brownish in the crude state, but can be bleached by animal charcoal, and forms small brilliant crystals very soluble in alcohol, sufficiently soluble in hot water to obtain it in a good crystalline state, requires about 1000 parts of cold water for solution, and has a strongly acid reaction to litmus. It is decomposed at about 240° C., appears to fuse, but gives off vapours, among which aniline can be detected. It is polybasic, and forms at least two series of salts: the neutral sodium salt $\text{C}_{32}\text{H}_{26}\text{N}_4\text{Na}_4\text{O}_{12}$ is very soluble and not crystallisable; the acid salt $\text{C}_{32}\text{H}_{27}\text{N}_4\text{Na}_4\text{O}_{12}$ is less soluble and crystallises well from water.

Decomposition in Strong Acetic Acid.

When the oxy-aceto-indigotin is heated with glacial acetic acid it is decomposed, yielding indigo-blue and brilliant yellow crystals. The decomposition here appears to be of a strictly intra-molecular character, as—



Analysis justifies the formula of the latter body, which has not been fully examined.

Enamelled Water-Baths with Ring Supports of Enamel.—B. Fischer (*Zeit. f. Angewandte Chemie*) proposes this material in order, in toxicological investigations, to exclude the possibility of traces of copper being introduced into the objects examined. Brass gas-burners have given rise to the introduction of traces of copper; whence the author proposes iron burners and glass lamps.

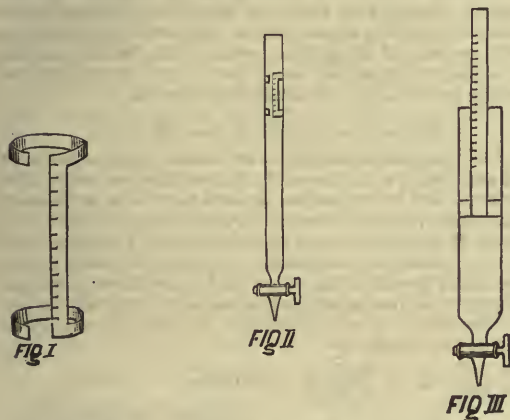
* Abstracted by the author from a communication to the Manchester Literary and Philosophical Society, Feb. 23, 1892.

IMPROVEMENTS IN BURETTES.

By ALEX. F. REID, of Bonshaw, Stewarton, N.B.

IN a former article (*CHEM. NEWS*, v. lxx., p. 68) I described an apparatus for measuring out liquids which may also be used as a burette. I will now describe an appendage to an ordinary burette which I find very useful when successive small quantities of solution are taken from the same burette. It consists of a sliding scale or vernier of sheet metal which slides on the outside of the burette.

It is shown on an enlarged scale in fig. 1 and on the burette in fig. 2.



An arrangement serving a similar purpose is shown in fig. 3, which consists of a burette of a rather large bore with a graduated tube inside. An india-rubber band is firmly fixed round the bottom of this tube so as to form a piston which slides inside the burette. By shoving down the inside tube after each titration the surface of the liquid is brought to the zero of the scale.

ILLUMINATING FLAMES.*

By Prof. VIVIAN B. LEWES, F.I.C., F.C.S.

Concluded from p. 114).

WITH this arrangement I was able to map out the temperatures existing in the flat flame, in which I had traced out the changes taking place in the constituents of the gas; and I found that the temperature rapidly rose from 500° C. half an inch above the burner, to a little over 1200° C. at the commencement of the luminous zone—the luminous edges having a temperature of 1216° C.; and these temperatures were further increased in the luminous zone until near the top of the flame 1368° C. was reached. This at once gives us the secret of the luminosity. From the mouth of the jet and up to a temperature of 1000° to 1200° C., we have the formation of acetylene from the original hydrocarbons; but the moment the requisite temperature is reached by the combustion of the hydrogen and the carbon monoxide, the acetylene decomposes, with a further rise of temperature, and the carbon heated to incandescence radiates heat and light.

If a luminous flame be cooled, its luminosity is at once diminished, and may be destroyed; while, as the propagation of flame requires a certain temperature, a further cooling will extinguish it. In the outer edge of a flame, the rapid inrush of air sucked into the flame so lowers the temperature that a thin envelope is rendered non-

luminous, the actions checked, and traces of the gas allowed to escape unconsumed by the extinction of the extreme limit of the flame; and delicate analysis shows that every luminous flame burning freely in air gives off distinct traces of carbon monoxide, acetylene, and even such highly-inflammable gases as methane and hydrogen.

Ever since the structure of flame has been noted and discussed, it has been accepted as a fact beyond dispute that the outer almost invisible zone which is interposed between the air and the luminous zone of the flame is the area of complete combustion, and that here the unburnt remnants of the flame gases, meeting the air, freely take up oxygen, and are converted into the comparatively harmless products of combustion, carbon dioxide, and water vapour, which only need partial removal by any hap-hazard process of ventilation to keep the air of a room fit to support animal life. The facts I have brought before you show that this is not the case; and they fully explain why gas is so oppressive in a badly-ventilated apartment.

It has always been the custom to speak of flame as built up of zones; and although there are no sharp lines of demarcation in the actions taking place which would warrant this, still three distinct portions are visible to the eye. If we divide the luminous flame into zones, it would be perhaps best looked upon as consisting of three, viz.:—

1. The inner zone, in which the temperature rises from a comparatively low point at the mouth of the burner to about 1000° C. at the apex of the zone. In this portion of the flame the constituents of the gas undergo various decompositions and interactions, which culminate in the conversion of the heavier hydrocarbons into acetylene—carbon monoxide being also produced; and these, with the products of combustion and residual hydrogen, pass into the next phase of action.
2. The luminous zone, in which the temperature ranges from 1000° C. up to a little over 1300° C. Here the acetylene formed in the inner zone becomes decomposed by heat, with liberation of carbon, which, at the moment of production, is heated to incandescence by the combustion of the carbon monoxide and hydrogen, and gives luminosity to the flame.
3. The extreme outer zone, in which, combustion being nearly completed, the cooling and diluting influence of the entering air renders a thin layer of the flame non-luminous, and finally extinguishes it. With ordinary coal gas, this results in the escape of traces of hydrogen, methane, carbon monoxide, and acetylene; while with a very rich gas unconsumed carbon also escapes.

This description of a luminous flame is of necessity far from complete, as it leaves out of consideration the interactions which lead to the formation of acetylene, and also the decompositions going on in the various parts of the flame between the products of combustion and the flame gases; but I think it marks a considerable advance in our knowledge of the main actions which lead to luminosity—the other interactions being at best subsidiary to it.

Having obtained a clear idea of the causes which lead to luminosity in flame, we are enabled for the first time to clearly understand the actions taking place in the atmospheric or Bunsen burner, the invention of which revolutionised our methods of heating by gas, and made coal gas one of the most important of our domestic fuels.

When it was first found that the admixture of a certain proportion of air with coal gas before combustion caused it to burn with a non-luminous flame, it was at once accepted, as an explanation of the phenomenon, that the extra oxygen so led into the inner cone of the flame, by causing complete combustion in the central zone, burnt up the carbon before it could be heated to incandescence, and so destroyed its light-giving power. Some years later,

* A Lecture delivered at the London Institution, February 18th.—From the *Journal of Gas Lighting*.

however, Knapp and others showed that, by mingling inert diluents, such as nitrogen, carbon dioxide, or even steam, with the gas before combustion, non-luminosity could be produced. It was then recognised that the diluting and cooling action of the nitrogen in air played an important part; and some observers held that it was this, and not the oxygen, which was the cause of non-luminosity.

On measuring the amount of air and of nitrogen respectively able to render a Bunsen flame non-luminous, they are found to be practically the same, while the quantity of oxygen present in the air used, when passed into the gas by itself, still gives a very luminous flame. This certainly looks as if it were the nitrogen that was doing the work. If this were so, the temperature of the flame rendered non-luminous by nitrogen should be the same as that of the flame rendered non-luminous by air; but, on testing these, the fallacy of such a supposition is at once exposed. This will be seen by the following table:—

Part of flame.	Temperatures existing in a Bunsen flame rendered non-luminous by—	
	Nitrogen.	Air.
$\frac{1}{2}$ inch above burner . .	30° C.	54° C.
1½ inches above burner . .	111°	175°
Tip of inner cone . .	444°	1090°
Centre of inner cone . .	999°	1533°
Tip of outer cone . .	1151°	1175°

These temperatures clearly show that a very considerable amount of combustion is due to the oxygen of the air, and make it perfectly manifest that both the oxygen and the nitrogen are acting in bringing about the loss of luminosity.

While working at these points, I found that if mixtures of nitrogen and oxygen, poorer in oxygen than air, were employed, it was practically only the nitrogen which acted—the diluting effect being so strong that the oxygen was prevented from taking any active part. With air, both act; while with mixtures richer in oxygen than air, the oxygen alone acts—the nitrogen being apparently unable to exercise any retarding influence. The same result is obtained if excess of air is mixed with the gas before combustion. If the quantity of air reaches a point at which the proportion of oxygen in the air is to the gas as 0.5 : 1, then the diluting influence of the nitrogen is lost, and the appearance of the flame becomes entirely altered. The normal Bunsen flame burns with a lilac-coloured inner and blue outer zone; but the moment the quantity of air admitted reaches the ratio mentioned, the flame becomes short and fierce, and the inner zone changes to a greenish colour,—the highest temperature in the flame at the same time increasing by nearly 100° C. Experiments show that the nitrogen acts in the normal Bunsen flame by so diluting and protecting the hydrocarbons that a far higher temperature is needed for their decomposition; and this action gives time for the oxygen of the air to consume them without liberation of carbon, and hence without luminosity.

In conclusion, I think that we may express the actions which lead to the loss of luminosity in the normal Bunsen flame in the following way:—

1. The chemical activity of the oxygen introduced in the air, which, by burning up the molecules of hydrocarbons before, in their diluted condition, they undergo decomposition, causes loss of luminosity.
2. The diluting action of the nitrogen of the air, which, by increasing the temperature necessary to bring about the partial decomposition of the hydrocarbons, prevents formation of acetylene, and in this way will, by itself, cause non-luminosity; and in the normal Bunsen flame it acts by doing this until destruction of the hydrocarbons by oxidation has taken place.
3. The cooling influence of the air introduced, which is able to add to the general result, although the

cooling is less than the increase in temperature brought about by the oxidation due to the oxygen in the air.

ON THE METHODS OF ESTIMATION OF THE FATTY BODIES IN VEGETABLE ORGANISMS.*

By WALTER MAXWELL.

THESE investigations have been conducted with the purpose of acquiring some further data showing the comparative proportions of matters which become separated from vegetable organisms by extracting with pure ether in variable durations of time. It has further been attempted to determine whether the whole of the substituted glycerides, or lecithines, do become separated by direct extraction with ether only.

The materials used in the work were pulverised to the greatest state of fineness, and the extractions were made with the Knorr extraction apparatus. The calculations are reduced to the standard of water-free material.

(a) The preliminary experiments, which were made in order to establish the proportions of the vegetable matters separated by the action of pure ether in different durations of time, are illustrated by the following results:—

Cotton-Seed.			
Time.	Weight of material.	Weight of extract.	Per cent.
Hours.	Grms.	Grms.	
8½	4	1.472	37.39
10	4	1.491	37.87
15	4	1.511	38.38

These results give the average of a great number of analyses. Although an increased amount of substance becomes separated with an increased duration of the period of extraction, the proportion is small; and it is not apparent that the greater duration of time causes an increase in the fatty bodies only, as other matters can be affected by a very protracted boiling. For these reasons it has been resolved to estimate the amounts of the fatty bodies separated by extraction with pure ether in a duration of fifteen hours.

In considering the estimation of the proportions of glycerides and substituted glycerides which are contained in the ether extract, the presence of other bodies, which have been removed with the ether, make it impossible, in the absence of an absolute analysis of the extract, to determine accurately the comparative relations of those fatty bodies. The ether extractions of plant matters contain variable proportions of cholesterin and of, in some instances, solid hydrocarbons, which may constitute several per cent of the extract. However, although the percentage of glycerides cannot be definitely estimated, the lecithines or substituted glycerides may be determined with absolute accuracy, as the estimation of these bodies rests upon the proportion of phosphorus present in the ether extract. The extract is combusted with mixed alkali salts, by which the phosphorus present in the organic form as lecithine becomes fixed as an alkali phosphate, and is then determined as magnesium pyrophosphate, and the latter body being multiplied with the known Hoppe-Seyler factor, gives the exact amount of lecithine.

A further series of extractions was made of the pulverised cotton-seed with pure ether for a period of fifteen hours, and the total extract determined. The proportion of lecithine contained in the extract was estimated by the method already given, the residue of the extract being

* From the *Proceedings of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.*

considered as glycerides and other bodies. The average of eight analyses gave the following results:—

Extract.. .. .	38·46 per cent.
Glycerides, &c. . . .	98·84 „
Lecithines	1·16 „

(b) It will be shown that the proportion of substituted glycerides stated, 1·16 per cent, does not represent the total lecithine present in the cotton-seed.

The observation was made simultaneously by Prof. E. Shulze, Zurich, and W. Maxwell, Harvard College, that the substituted glycerides do not become wholly separated by extraction with ether, even in a great duration of time. It was found that if the material which had been already extracted with ether were further extracted with absolute alcohol another portion of substituted glycerides was obtained, which in most instances was greater than the amount separated by the ether. The process of the alcohol extraction consisted in merely extracting the material already treated with ether, and evaporating off the alcohol and re-extracting the alcohol extract residue with ether. The reason for taking up the lecithines out of the alcohol extract was that it has been observed that those lecithines which were originally insoluble in ether became soluble in that menstruum when previously acted upon by alcohol. The use of ether was further made in order to avoid any small portion of inorganic phosphates which might have been removed from the vegetable material by alcohol. It was found, however, that only a mere trace of mineral phosphates had been separated by the action of the alcohol.

The amount of the ether extraction of the alcohol extract in one hundred parts of the vegetable material with the proportion of lecithines was as follows:—

Extract	2·3 per cent.
Lecithines in extract	16·6 „

A further comparison indicates the following:—

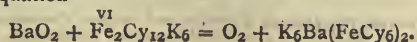
	Extract. Per cent.	Lecithines. Per cent.	Glycerides, &c. Per cent.
Ether	38·46	1·16	98·84
Ether and alcohol.	40·76	2·30	97·69

The proportion of lecithines to the total fatty bodies contained in the cotton-seed is very small, yet it is seen that about 50 per cent of those substituted glycerides are left in the material after extraction with ether for a period of fifteen hours. If certain other varieties of seeds be considered, such as the legumes, pea, vetch, bean, Boston bean, &c., it is found that the total ether and alcohol extracts of those seeds are composed of lecithines varying from 25 to 45 per cent. It is thus apparent that in the examples of seeds given as far as 20 per cent to 25 per cent of the total fatty bodies can remain unseparated and undetermined when the material is extracted with ether only.

THE BEHAVIOUR OF BARIUM PEROXIDE WITH METALLIC SALTS.

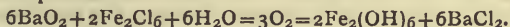
By H. KWASNIK.

IN 1890 the first assistant at the Pharmaceutical Institute at Breslau, Dr. Kassner, published two methods for the volumetrical determination of potassium ferricyanide and the peroxides of the alkaline earths, using for the former the reaction of hydrogen peroxide and potassium ferricyanide, and for the latter that of barium peroxide and potassium ferricyanide. This latter reaction took an unexpected form, since the total oxygen is liberated as such without the formation of ozone or hydrogen peroxide, but with a reduction of the ferricyanide according to the equation—



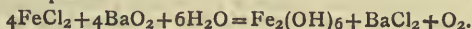
The process takes place so definitely that it is sufficient to cover equivalent quantities of barium peroxide and potassium ferricyanide with cold water in order to obtain at once a copious evolution of pure oxygen. Why obtain from 2·3 grms. of barium peroxide at 75 per cent about 240 c.c. of oxygen, whilst theory requires 236 c.c.?

In connection with this I made the observation that ferric chloride with barium peroxide likewise produces a copious liberation of oxygen, but here there ensues no reduction of the ferric salt, and consequently only half the oxygen of the barium peroxide is liberated, according to the equation—



At the instigation of Herr Poleck I have pursued this subject further, and have studied the action of a great number of metallic salts upon barium peroxide, whereby I have arrived at results which were novel and not devoid of interest.

On repeating the experiment above described, that only the half of the oxygen of the barium peroxide is given off, no trace of a ferrous salt is formed, nor is there any formation of hydrogen peroxide or of ozone. It was further found that all the ferric salts, sulphates, nitrates, acetates, &c., act in the same manner, and that the behaviour of the ferrous salts is similar, though more tedious, since the escaping oxygen first peroxidises the ferrous compound, after which ensues the liberation of oxygen, in this case only to the extent of one-fourth part, according to the equation—



As for the action of metallic salts in general upon barium peroxide, the salts of potassium, sodium, lithium, ammonium, calcium, strontium, and barium have no action, not the slightest escape of gas occurring even on the application of a gentle heat. Heating up to 100° must be avoided, since under such circumstances barium peroxide alone evolves oxygen.

The magnesium salts react, but the development of gas begins only after some time, whilst salts of zinc and cadmium react more rapidly, and salts of cobalt and nickel produce immediately a strong liberation of oxygen. In the latter case the mixture takes the colour of the hydroxide concerned. Salts of manganese, chromium, and aluminium behave similarly to ferric chloride; salts of copper effect an abundant escape of oxygen without reduction; whilst the above mentioned salts liberate half the oxygen combined with the barium, with a simultaneous formation of hydroxides, the group of noble metals have a decidedly different behaviour.

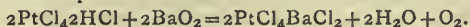
Mercury salts experience at once a decided reduction with barium peroxide. Oxygen is given off, and the mixture becomes constantly darker; metallic mercury is separated as a blackish grey powder, which, on treatment with dilute hydrochloric acid, sometimes coalesces into metallic globules, $\text{HgCl}_2 + \text{BaO}_2 = \text{BaCl}_2 + \text{Hg} + \text{O}_2$.

The behaviour of the silver salts is quite similar. They yield a black-grey deposit with a copious evolution of oxygen. The precipitate dissolves in ammonia only to a very slight extent, occasioned by small quantities of barium oxide; after removal of the excess of barium peroxide by treatment with dilute hydrochloric acid metallic silver remains behind as a grey powder.

In a similar manner metallic gold is separated from gold salts as a brown-black powder. In very dilute solutions of gold, and if the reaction is caused to be as slow as possible, the same phenomena are observed as on the reduction of gold salts by oxalic acid. The liquid first takes a blue tone, and after some time the gold is deposited upon the sides of the vessel as a brilliant mirror.

Whilst these reactions take place definitely platinum chloride shows a different behaviour. It is not reduced to metal, although there is here an escape of oxygen. The liquid remains yellow even on the addition of a large excess of barium peroxide,—a result which is not modified by heat. The filtrate was evaporated down on the water

bath and precipitated with absolute alcohol. The light, orange-coloured precipitate was washed with alcohol, then dissolved in water and re-crystallised by evaporation. The crystals were $\text{PtCl}_4\text{BaCl}_2 \cdot 8\text{H}_2\text{O}$. The platinum found was 28.24 per cent, whilst theory required 28.73 per cent. In these experiments the ordinary platinum chloride solution of laboratories was used containing PtCl_4HCl , which easily explains the formation of the double compound—



It is perfectly indifferent in its behaviour with platinum peroxide; the behaviour of the other platinum double salts of alkalies and alkaline earths was identical, no platinum being reduced from any of them. But the action of barium peroxide is quite different upon pure platinum chloride, and upon its double compounds with the salts of metals which disengage oxygen from barium peroxide. If a molecule of the compound PtCl_4HCl is mixed in an aqueous solution of two molecules silver nitrate, there separates out a mixture of platinum chloride and silver chloride, PtCl_4AgCl , and of silver chloride, whilst there is formed at the same time a reddish-yellow solution of platinum chloride free from silver. If this mixture is exposed to the action of barium peroxide, oxygen is given off and black flocks are deposited, whilst if an excess of barium superoxide is added, the supernatant yellow liquid is decolourised, proving the decomposition of the platinum chloride. In fact, after the excess of barium precipitate has been removed by means of dilute hydrochloric acid, the precipitate consists merely of metallic platinum and silver.

The fact that silver chloride, insoluble in water, is reduced by the action of barium peroxide, with the elimination of its entire quantity of oxygen, led to an examination of other insoluble metallic salts. As a result of the examination of insoluble sulphates, carbonates, phosphates, arseniates, it was found that the selection of the acid had no influence upon the course of the reaction; oxygen was given off in every case with a formation of the respective hydroxides, though the action is naturally here slower. Whilst in some of these insoluble salts the reaction must be initiated by the application of heat, in others the process takes place easily, as in ferrous phosphate, copper carbonate, mercurous chloride, and silver chloride. The reduction of silver chloride by this method is easily effected.—*Ber. Deut. Chem. Gesell.*, xxv., p. 67.

AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

FOURTH MEETING, 1892, HOBART.

The grand vision of a pan-Britannic Association for the Advancement of Science has melted away in conflict with the stern realities of time and space. Few, indeed, of our African, Indian, not to speak of Australian, colleagues could spare the time for a yearly or even decennial visit to Britain. Even if the gathering were to take place, say, at Cape Town, the inconvenience would be merely transferred, not abrogated.

Such being the case, we must unfeignedly rejoice at the rise and progress of the Australian Association. This itinerant body is founded on the lines of the British Association. Its meetings are held by rotation in each of the Australasian Colonies. It has its sections, its presidential addresses, its meetings for reading and discussing papers, its excursions, its receptions and garden parties, and even its "science sermon." But along with the general features of its forerunner, it has adopted a few of the defects of the latter, and has called into being some undesirable features, from which our old "B A" has been free. The number of sections has been increased. We see under A

"Astronomy, Mathematics, Physics, and Mechanics." It is undeniable that not a few astronomical phenomena may be studied to more advantage in Australia than in Europe. But mathematics, physics, and mechanics present no such local facilities. Whatever could be effected in those sciences in Australia might be done quite as well in Britain, France, or Germany.

With section B (chemistry and mineralogy) the case is different. Numbers of Australian plants—and some animals—contain proximate principles which demand and merit thorough investigation. Nor have all the local minerals been fully explored.

In section C (geology and palæontology) the state of affairs is very similar. But the most tempting and, doubtless, the most remunerative field is presented by section D (biology). We must say that here the ground has been merely scratched. As many of the plants and animals are the friends of man, and others his deadly enemies, there are here practical reasons for careful study. Concerning section E (geography) there is still scope for work under the Southern Cross.

Section F (economic and social science, and statistics) has been one of the defects of the British Association. Statistics cannot be regarded as a science, but as a method. Economics slide too easily into party politics, and meet with ample scope in chambers of commerce, municipal bodies, &c. Sociology is not yet constituted as a science. All of us will remember the "social science congresses" in England, which, it was drily said, were gatherings "of men who ought to have been women, and of women who repined that they were not men."

Section G (anthropology) might, perhaps, have been included under D.

For sanitary science and hygiene (H) there is, we fear, too great a need. It is humiliating for the British Empire and the British races, that both in Australia and South Africa we have successfully acclimatised typhoid fever and diphtheria!

Section I (literature and fine art) has been found in England a dangerous neighbour to science. In the so-called Literary and Philosophical Societies of England, e.g., that of Liverpool, science would be benefitted by a process of dissociation. But why, we would ask, is there not a section for agricultural science?

Section J (architecture and engineering) might be usefully divided. Engineering might be combined with section A, and architecture might rank as a fine art under section I.

The projected excursions, especially those to the silver fields and tin mines, and the salmon ponds, promise to be intensely interesting. It is decidedly exceptional to find good silver deposits in the Eastern Hemisphere. The Mount Bischoff Tin Mine asserts a claim to be the largest tin mine in the world. At least, it has turned out upwards of 53,000 tons of tin, employs regularly 380 men and boys, and has the cardinal virtue of paying good dividends.

We have not yet received copies of the Presidential Address and of the papers read before the sections, but some of them, as far as we can judge from the titles, promise to be exceedingly important. We wish the Australasian Association a long and splendid career.

Dispersion of Prism-Spectroscopes.—G. Guglielmo. —The author, in order to increase the dispersion of such spectroscopes, places in front of the lower halves of the object-lenses of the collimator and the observing telescope glass mirrors silvered on their front sides, slightly inclined towards the perpendicular. Thus a part of the light is several times transmitted backwards and forwards through the prism, and the dispersion is considerably increased. A great loss of light is inevitable.—*Rendicon. de la Reale Acc. dei Lincei*, vi., 195.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 26, 1892.

Prof. W. E. AYRTON, F.R.S., Past President, in the Chair.

PROF. S. P. THOMPSON, F.R.S., read a paper "*On Modes of Representing Electromotive Forces and Currents in Diagrams.*"

The author said he had found it advantageous in some cases to depart from the usual methods of representation, and he now brought the subject before the Society in order to have it discussed and improvements suggested.

To indicate the direction of currents in wires seen end-on, Mr. Swinburne had used circles with and without crosses, but no symbol had been suggested for wires not conveying currents. He (Prof. Thompson) thought the plain circle should be used for inactive wires. A circle with a dot in the middle could then be used to indicate that a current was flowing towards the observer, and a circle with a cross in it to represent a wire conveying a current away. These meanings could be recalled by considering the direction indicated by an arrow; the dot showing the tip of the arrow, and the cross the feathers.

Some method of distinguishing between E.M.F. and current was required. For this, he proposed to use thin stemmed arrows with feathers for E.M.F.'s, and thick stemmed ones without tails for currents. In the case of electrical transmission of energy, this convention had the important advantage that where the two arrows had the same direction, energy was being given to the system, and where the arrows were opposite, energy was leaving it.

Mr. Maycock, he said, had recently published a simple rule for finding the direction of magnetic force due to a current of known direction in a wire. Grasp the wire with the right hand, the thumb pointing in the direction of the current; the fingers will then encircle the wire in the direction of the magnetic force. Dr. Fleming's well-known rule for induced currents was also a *right-hand* rule, but as it referred to the direction of *currents*, another rule was necessary when considering motors. By making the rule refer to E.M.F.'s only, one rule was required for generators and motors.

For alternating currents, the author found it convenient to draw polar curves analogous to Zeuner's valve diagrams. Suppose a line, OP (Fig. 1), representing the

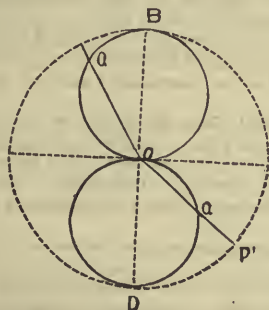


FIG. 1.

maximum value of an E.M.F. or current whose magnitude is a sine function of the time, to revolve at uniform velocity about O; the intercepts, OQ and OQ', &c., cut off by circles, OQB, OQ'D, will represent the magnitudes at the times corresponding to the positions OP and OP'.

The effect of lag can also be represented in such diagrams.

In cases where the variables are not sine functions, the curves OQB and OQ'D are no longer circles. Polar diagrams, representing the E.M.F. and current curves obtained by Prof. Ryan in his transformer experiments were exhibited, and a working diagram illustrating the changes in three phase currents was shown.

To show the directions of induced E.M.F.'s in diagrams of dynamos and motors, diagonal shading of the pole faces was sometimes convenient; the lines over north poles being drawn from left to right downwards in the direction of the middle stroke of the letter N, and those over south poles from left to right upwards. A conductor passing over a north pole from left to right would have an E.M.F. induced in a downward direction, as indicated by the slope of the diagonal lines. This method of representation was used to show the ways of connecting up multipolar drum armatures, the winding being supposed cut along a generating line, unwrapped from the core, and laid out flat in the manner adopted by Fritzsche.

In connection with armatures, the author said a formula had been published by means of which the nature of a winding consisting of a given number of convolutions and to be used with a given number of poles could be predetermined. This, he thought, would be very useful in practice.

Mr. BLAKESLEY said the old method of representing alternate current magnitudes by means of the projections of revolving lines seemed preferable, for it left no ambiguity as to the directions of the quantities. The method of shading the poles also required that the direction in which the diagram was to be viewed should be known before the direction of the E.M.F. could be determined.

Mr. SWINBURNE suggested that the author might use a bow to represent E.M.F., and an arrow for current. He was glad to see that Prof. Thompson recognised the differences in dynamos and motors, and approved of the view that mnemonic rules should refer to E.M.F., and not to current. The diagrams of drum windings would be very useful, and he hoped the author would make the subject clear to ordinary workmen in the next edition of "*Dynamo-Electric Machinery.*"

Prof. PERRY considered it undesirable to use the polar curves for anything but circles. In his opinion, it was not sufficiently known that any curve can be split up into a series of sine curves, and each component dealt with separately, the separate results being added together in the end.

Mr. SWINBURNE pointed out that before one could analyse a curve in this way, the curve must be known, and would probably have to be determined experimentally. If means for finding one curve are available, any other required curve could probably be found by the same apparatus; hence there was no need for analysis.

Prof. PERRY remarked that experiments could not be made on a machine before the machine was built; whereas the E.M.F. curve could be pre-determined from its design. By analysis, its current curves when working under various conditions could be found.

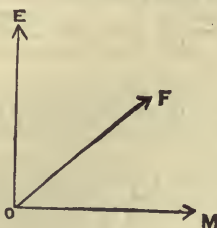


FIG. 2.

Prof. AYRTON, referring to the mnemonic character of the modes of representation described by Dr. Thompson suggested that the symbols in the author's book should

be more mnemonic. He himself was in the habit of using large letters for currents, and small ones for resistances; A and a for the armature, S and s for series, and Z and z for the shunt, currents, and resistances respectively, and σ and ζ for the series and shunt turns. He also found the following "electromotive force" rule very convenient:—Draw three rectangular axes, O M, O F, and O E, as shown in Fig. 2. If then, O F represents the direction of the force (magnetic), O M that of the motion, then O E shows the direction of the induced E.M.F.

Dr. THOMPSON, in replying, said he thought Mr. Blakesley had misunderstood what had been said, for no ambiguity existed.

In describing the windings of armatures, difficulty arose from want of proper names for the various elements, and in his forthcoming work suitable names had been given. To Prof. Ayrton he pointed out that in his book he (Dr. Thompson) had used mnemonic characters; for r_a , r_s , and r_m , represented the resistances of the armature, shunt, and series magnet coils respectively. The symbol I for current had also been recommended for adoption by the Frankfort Committee. He objected to Greek letters except for specific quantities, such as angles, specific inductive capacities, refractive indices, &c.

He appreciated the simplicity of Prof. Ayrton's E.M.F. rule, but thought it would be better to rotate O E and O F through a right angle about O M, thus giving Fig. 3.

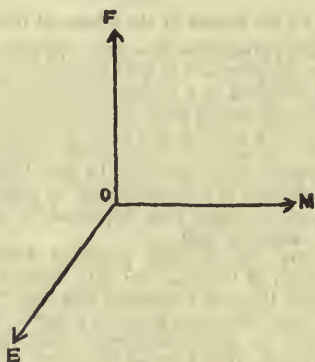


FIG. 3.

A paper on the "Flexure of Long Pillars under their own Weight," by Prof. M. FITZGERALD, M.B., was read by Mr. Blakesley. The subject of upright pillars fixed at the base and free at the top is treated mathematically, the differential equation being integrated in two series, involving ascending powers of the variable. Putting L for the ratio of length to diameter, the result, when applied to thin steel tubes and rods, for which Young's Modulus is taken as 12,000 tons per square inch, show that the limiting height (in feet) of pillars which can stand without bending is given by $H = \frac{15 \times 10^6}{L^2}$ for tubes and $H = \frac{7.5 \times 10^6}{L^2}$ for rods.

If L = 100 the maximum height of a tube is 1500 feet, the diameter being 15 feet. For wires, L may have larger values, and the limiting length of a No. 28 B.W.A. steel wire is about 10 feet.

In the case of pillars whose neutral axes are constrained to be vertical both at top and bottom the results show that a definite ratio must exist between the bending moments producing the constraint.

A paper on "Choking Coils" by Prof. Perry, F.R.S., and a Description of the Uses of Rice's Choking Coils for Regulating the Brilliancy of Incandescent Lamps, by Mr. Hammer, were postponed until next meeting.

NOTICES OF BOOKS.

A Treatise on Chemistry. By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Vol. III. *The Chemistry of the Hydrocarbons and their Derivatives; or, Organic Chemistry.* Part VI. (8vo., pp. 582). London and New York: Macmillan and Co.

THE authors of this work are still grappling with their enormous task, the end of which is not yet. The progress of organic chemistry is now so rapid that it is not easily overtaken. The groups of compounds here described are the indene, the naphthalene, the methylnaphthalene, the dimethylnaphthalene, and the ethylnaphthalene groups; then follow the naphthalene derivatives containing more than twelve atoms of carbon; the naphthindole derivatives; acenaphthene group; the pyrene, diphenyl, methyl-diphenyl, dimethyldiphenyl, and ethyldiphenyl groups; the derivatives of diphenyl containing more than fourteen atoms of carbon; the azo dyes of the diphenyl group; the fluorine, phenanthrene, retene, fluoranthene, phenylnaphthalene, chrysene, dinaphthyl, diphenylbenzene, and triphenylbenzene groups.

The chief practical interest of a large proportion of the compounds here described depends on their proposed or possible applications in dyeing and tissue-printing. Not, indeed, that all these colouring-matters are in actual use. Many of them have been abandoned on account of some undesirable feature, others because they are too expensive, and others, again, simply because they present no well-marked advantage over their rivals.

Mention is made of the method of producing azo-dyes directly upon the fibre—a process which is ascribed, as we believe correctly, to Holliday. Whether analogous methods will become extended experience must decide.

Among the many curious facts here mentioned, we may refer to the poisonous character of α -hydrojuglone, a compound obtainable from the green shells of the walnut. Even goats are found to perish if they indulge in a raid upon walnut trees.

Many of the naphthalene compounds are mentioned as giving off exceedingly offensive odours. This property is not to be despised, since such compounds may prove exceedingly valuable in repelling those insect parasites with which our crops and even our persons are so persistently beset. We should recommend careful research in this direction.

A very useful feature of the book is that, as in former volumes, the reader is constantly referred in foot-notes to original memoirs, to patent specifications, &c., where the fullest details may be found.

The index is very copious, and, so far as we have been able to test it, remarkably correct.

The work, as a whole, is beyond question the best systematic compendium of chemistry of the age.

Chemical Calculations. With Explanatory Notes, Problems, and Answers. Specially adapted for Use in Colleges and Science Schools. By R. LLOYD WHITELEY, F.I.C. With a Preface by Prof. F. CLOWES, D.Sc., F.I.C. London: Longmans, Green, and Co. Small 8vo., pp. 100.

IT has been confessed that one main reason for the delay in the introduction of the experimental sciences into English schools and universities is the fact that they do not lend themselves readily to the examinational system of education which we have acclimatised from its native China. Works like the present seem, therefore, to have met with the readier acceptance among us because they enable the student to say that he is learning chemistry, whilst at the same time he is doing little to cultivate his powers of observation and of tracing phenomena to their sources.

Mr. Whiteley's treatise, though good of its kind, is

avowedly and intensely examinational. Says Prof. F. Clowes, with subtle irony, "it is safe to predict that it will be found to meet the requirements of candidates for the various university, professional, and Government examinations which now serve as tests of chemical knowledge." How illusive such tests must necessarily prove has been shown over and over again. Suppose two students, one of whom is strikingly successful in answering the questions here given, and the other as signally unsuccessful, we submit that both may still be equally competent or equally unable either to extend the boundaries of the Science or to apply its laws to industrial purposes.

Royal University of Studies at Rome. Chemical Institute. Researches executed in the Scholastic Year 1890—1891. (Regia Università degli Studi di Roma. Istituto Cnifico. Ricerche eseguite nell'anno Scolastico 1890—1891). Rome: Printing Office of the Lyceum Academy.

THIS volume, for which we are indebted to the courtesy of Prof. Cannizzaro, affords satisfactory proof that Italy is not backward in chemical research. Some of the memoirs here contained are exceedingly elaborate, and bring to light very interesting results. We may especially mention a paper by F. Marino-Zuca on a new alkaloid extracted from a species of chrysanthemum, or perhaps we should rather say of pyrethrum. From the remarkable insecticide power of the flowers of this plant, known in trade as insect-powder, we might infer the presence of some active principle. The author has, in fact, isolated a paraffin, a new cholesterine, a glucoside, and an alkaloid which he has named chrysanthemine, and which is the chief subject of the memoir; pure chrysanthemine, a colourless syrup or colourless needles grouped in rosettes. The alkaloid may be heated for a long time on the water-bath, but above 100° it begins to decompose, giving off an odour of trimethylamine.

The aqueous solution has an alkaline reaction, both with turmeric and litmus papers. For its volumetric determination methyl-orange is preferable. The base is soluble in ethylic and methylic alcohol; it is insoluble in ether, chloroform, and benzene. Its salts behave as follows with the ordinary reagents for alkaloids. With bismuth and potassium iodide it gives a flocculent orange-yellow precipitate, which, on agitation, becomes crystalline and of a bright red colour. With mercury potassium iodide it yields a yellowish-white precipitate; with platinum-sodium iodide a brown precipitate; with gold chloride a yellow crystalline precipitate, which dissolves if heated and re-crystallises on cooling. With platinum chloride, mercuric chloride, picric and tannic acids, no precipitate is produced. Chrysanthemine is completely inactive in polarised light. Physiologically it is inoffensive. The author has experimented upon frogs, rabbits, mice, and dogs, and always found it completely inoffensive. Its formula seems to be $C_{14}H_{28}N_2O_3$.

Two papers treat of hydrogen peroxide; one by G. Giorgis examines the action of this compound and of water saturated with carbonic acid upon metallic magnesium. It results from his experiments that pure magnesium is oxidised in a minimum quantity by neutral hydrogen peroxide. The oxide resulting is scarcely soluble in pure water, whence the phenomena observed by Weltzier must probably have been due to some impurity in the materials. Pure water and oxygenated water saturated with carbonic acid convert magnesium into neutral carbonate. The aqueous solution of carbonic acid acts like a true acid.

A. Piccini has studied the action of hydrogen peroxide upon some oxyfluorides and fluorides. Santonine has also been made the subject of two elaborate papers, the one by P. Gucci and E. Grassi-Cristaldi, and the other by L. Francesconi.

Some of the contributors to this volume introduce

numbers into the names of compounds, such as "On the hydrogenation of 1 phenyl, 4 methyl, 5 ethyl pyrazole, and on 1 phenyl, 3—5 dimethylpyrazole." Such a mode of notation can scarcely fail to prevent difficulties.

CORRESPONDENCE.

THE EDUCATION OF THE STUDENT.

To the Editor of the Chemical News.

SIR,—The communication of "F. G. M." in the last issue of the CHEMICAL NEWS has expressed the meaning of my letter exactly.

It would be a pity, I think, if a young chemist, after spending years in studying the science, should jump at the first opening that occurs, no matter what it be.

This, then, is where the difficulty comes in: which of the many branches of chemistry is advisable, speaking from a worldly as well as a scientific point of view?—I am, &c.,

W. S.

John Street, Glasgow.

GOLD IN SEA WATER.

To the Editor of the Chemical News.

SIR,—Recent paragraphs that have appeared in the press relating to the presence of gold (and other metals) in sea water, and referring to a patented electrolytic process or processes for obtaining such metals, include a statement that the quantity of gold has been estimated at one grain to the ton of sea water. Presumably, although my name does not appear in the paragraphs that friends have sent me, the statement of the proportion of gold in sea water is based upon my paper that appeared in the CHEMICAL NEWS (vol. xxvi., p. 159).

Not having the original paper at hand, I refer to "Watts's Dict. of Chem.," vol. vii., Second Supplement, and there find that my statement was that "the quantity is certainly less than one grain in a ton" of gold in sea water. I did not make any such statement as is now going the round: that a ton of sea water contains a grain of gold. I simply stated that proportion as an extreme possible limit.

I am the more particular to emphasize my old position of non-committal to a quantitative estimate of the gold in sea water, as experiments I have been for some months past making on sea water supplied from Lowestoft in kegs by the G. E. Ry. Co., convince me that the proportion of gold is not only much less than my former superior limit, but is also greatly less than I had supposed it to be. Nevertheless, of the presence of gold in sea water I have gained additional evidence: but a quantitative result I have not yet obtained.—I am, &c.,

E. SONSTADT.

Cheshunt, March 8, 1892.

The Preparation of Lackmoid.—M. Schaerger (*Schweitz. Wochenschrift Pharmacie und Chem. Zeitung*).

—The author causes sodium nitrite, without the addition of water, to act upon resorcin at a temperature not exceeding 110°. The product is dissolved in a little water, and freed from undecomposed resorcin by agitation with ether. Lackmoid forms a clear solution in water and dilute alcohol in any proportion. If the aqueous solution is mixed with acid, the red colouring-matter which results can be removed by agitation with ether. This character distinguishes lackmoid from the tincture of litmus.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 8, February 22, 1892.

Preparation of Amorphous Boron.—Henri Moissan.—The author uses for this purpose the action of metallic magnesium in powder upon an excess of boric acid, which must be absolutely dry. The product is a mixture of boron and of magnesium borate and boride. The borate and the chief part of the boride are eliminated by successive washings with acids. By a repeated treatment with boric acid in a state of fusion he oxidises the remainder of the boride, and after washing obtains amorphous boron, containing merely a very slight proportion of nitride. If it is desired to avoid the presence of these traces of boron nitride, we must operate in an atmosphere of hydrogen, or line the crucibles with titanite acid, and under these conditions the amorphous boron is obtained pure.

New Researches on the Monochlorised, Monobromised, and Monocyanised Aceto-acetic Ethers.—A. Haller and A. Held.—These researches show that, according to the mode of preparation, and therefore according to the reactions brought into play, the monohalogenous aceto acetic ethers appear sometimes as compounds α , sometimes as γ derivatives, and sometimes as a mixture of substituted α and γ derivatives.

Researches on the Realisation of Spheroidal State in Steam-Boilers.—A. Witz.—Boutigny's phenomenon, the so-called spheroidal state of water, is not produced in boilers when the plates are in a state of incipient redness, but the evaporation reaches then a degree of activity which merits especial attention.

The Solubility of Tricalcic and Bicalcic Phosphate in Solutions of Phosphoric Acid.—H. Causse.—It appears that tricalcic phosphate dissolves in solutions of phosphoric acid to a much greater extent than bicalcic phosphate. The cause of this difference seems to reside in an equilibrium established between three factors—water, phosphoric acid, and monocalcic phosphate. The water seems to play the principal part; it distributes its action between the monocalcic phosphate and the phosphoric acid, and everything depends on the proportion of these two compounds.

On the Stereochemistry of Diacetyltartaric Acid. A Reply to a Communication by M. Le Bel.—Albert Colson.—A controversial paper which does not need to be reproduced.

Thermic Study of Sodium Isopropylate.—M. de Forcrand.—A thermo-chemical paper, which does not admit of useful abstraction.

On Tartronic Acid and the Potassium and Sodium Tartronates.—G. Massol.—The quantities of heat evolved by oxymalonic acid are greater than those disengaged under the same conditions by malonic acid. This result is conformable to those which the author has previously obtained on comparing malic and tartaric acids (oxysuccinic) with succinic acid.

Specific Weight of Textile Fibres.—Leo Vignon.—For determining these specific gravities the author uses the hydrostatic balance, employing instead of water pure benzene. Condensed gases were eliminated by means of a reduced atmospheric pressure. The specific gravity of cotton is given as 1.50; that of wool as 1.30, and that of silk in different states of preparation as 1.33. "Loaded" or weighted silks were found with specific gravities as high as 2.01.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., No. 1, January 5, 1892.

The Molybdc Reaction of Oxygenated Water.—G. Denigès.—In the *Bulletin*, Series 3, Vol. vi., p. 22, M. Crismer enters into a discussion, historical and chemical, to prove that Schöne and himself had previously described this reaction, that it is untrustworthy and not sensitive, and that it is advantageous to employ his reagent (citric acid and ammonium molybdate). Crismer has, indeed, criticised about the end of 1888 the use of ammonium molybdate acidulated with sulphuric acid for the detection of oxygenated water. M. Denigès has shown that strongly sulphuric solutions have none of the disadvantages recognised by M. Crismer in solutions merely acidulated. M. Denigès therefore still recommends the following formula:—Dissolve 10 grms. ammonium molybdate in 100 c.c. water, and add, little by little, whilst refrigerating, 100 c.c. pure sulphuric acid. The liquid always takes a blue colour after some time, but the colouration disappears on heating. It is most sensitive at 60–80°. In practice we heat in a test-tube a few c.c. of the reagent, and add a few drops of the liquid in which oxygenated water is to be detected. In presence of this body there appears at once a yellow colour, which may even reach a deep orange. No other acid is to be used.

The Rotatory Power of Silk.—Leo Vignon.—This paper has been already noticed.

A Synthesis of Non-saturated Nitriles.—Edmond Fiquet.—The author has studied the action of metatoluic, cinnamic, and ethylic aldehyds upon cyanacetic acid. He points out that the ether obtained by Mr. Carrick, of the University of Leipzig, by the action of ethyl cyanacetate upon benzylic aldehyd in presence of sodium is not susceptible of the same transformation as that obtained by the author.

On Thiopinacone.—W. Spring and J. van Marseville.—This compound has a composition answering to the formula C_8H_8S .

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 69.

This issue contains no chemical papers.

MEETINGS FOR THE WEEK.

- MONDAY, 14th.—Medical, 8.30.
— Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).
TUESDAY, 15th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Peru—Its Commerce and Resources," by F. A. Pezet.
WEDNESDAY, 16th.—Society of Arts, 8. "Iceland," by Tempest Anderson, M.D.
— Meteorological, 7.
— Microscopical, 8.
THURSDAY, 17th.—Royal, 4.30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "The Progress of Romance in the Middle Ages," by Prof. W. P. Ker, M.A.
— Chemical, 8. "The Conditions which Determine Combination between the Cyanides of Zinc and Mercury and the Composition and Properties of the Resulting Double Salt," by Prof. Dunstan.
— "A Lecture Experiment to Illustrate the Phenomena of Coal-Dust Explosions," by Professor Thorpe, F.R.S.
— "The Ketone Formed by the Action of Dehydrating Agents on Camphor," by Dr. Armstrong and Dr. Kipping.
— "Platinum Tetra-chloride," by F. Pullinger, B.A.
FRIDAY, 18th.—Royal Institution, 9. "Modern Satire in Black and White," by George Du Maurier.
— Quekett Club, 8.
SATURDAY, 19th.—Royal Institution, 3. "Matter: at Rest and in Motion," by the Right Hon. Lord Rayleigh, D.C.L., F.R.S.

THE CHEMICAL NEWS.

VOL. LXV., No. 1686.

REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg.

Introduction.

UNDER this head we propose to give a series of papers concerning the modern crucible steel manufacture in Russia, describing also the preparation of projectiles, pattern castings, tool steel, locomotive tyres, &c.

In 1889 we superintended the erection of the crucible steel department of the Poutiloff Iron and Steel Works, St. Petersburg. The first thing built was a Siemens gas furnace with three compartments for ten crucibles each, and a muffle furnace for heating sixty crucibles at one time.

There was one gas-producer of the ordinary type, but only two compartments were fired, the other two always ready in case of some accident with the former. The consumption of coal (English) was 1·93 poods per pood of steel melted (1 pood = 40 pounds = 36·11 English pounds). We found that the best height for the layer of the coal was 32 inches, counting from the fire-grate. The run of the gas was then steady and quite sufficient for the melting of steel in due time.

During the making of hard steel (projectiles and tool steel) we had five castings per twenty-four hours, stopping melting on the evening of Saturdays and charging the crucibles again on Sunday mornings. But when steel castings were demanded, or medium hard steel was ordered, we made only four heats per twenty-four hours.

I had a great difficulty with the workmen, the crucible Siemens furnace being not in use in St. Petersburg. The Olouchoff Steel Works here, for the manufacture of their steel, principally for ordnance, use coke crucible furnaces and Siemens-Martin steel. I succeeded in getting some workmen formerly employed at these works, and in some two to three months my department went smoothly on.

Perhaps it may be interesting to state the amount of wages paid to the workmen. Such information respecting Russia is very scarce abroad. Each shift comprised one head melter, three crucible drawers, and one fireman for the muffle furnace and for the opening of the covers of the gas furnace during the casting. The ordinary workmen for bringing the crucibles to the moulds were in numbers according to the character of the cast made, and comprised the workmen employed in the department for other purposes (breaking cast-iron, shearing the raw materials, crucible making, &c.). Finally, the shift of the gas-producer consisted of one head workman and two firemen. The wages are in paper roubles.

Gas Furnace.

Head workman	2·40
Crucible drawer	1·60
Fireman (muffle furnace)	1·00

Gas Producer.

Head workman	1·15
Fireman	1·00

The workmen employed for bringing the crucibles on the average received 0·95 rouble. The piece-work wages for other work was as following (paper roubles):—

	Per pood.
Modelling castings	0·60
Cleaning	0·25
„ ingots	0·10
Shearing raw material	0·03
Breaking cast-iron	0·02
Cleaning used crucibles from slag	0·10

The charge of each crucible comprised sixty-two pounds of raw material. This material consisted of the following:—(a) Swedish cast-iron, brand "three lilies"; (b) Swedish iron, brand J. M.; (c) blister steel, Russian and Swedish (W.F.); (d) puddled steel, Russian (Beloretz Works); (e) acid and basic steel of the own Works; (f) old crucible steel from the market; (g) German ferro-manganese; (h) silicon pig-iron; and finally (i) silicon spiegel. The last two materials came also from Germany.

I prepared myself the ferro-aluminium (10 per cent of aluminium) by using cast-iron of good quality and pure aluminium received from the Pittsburgh Reduction Company, U.S.A. It contained, according to our analyses, 97·5 per cent of the metal.

I propose to deal in my next paper with the analyses of raw materials and the manufacture of crucibles. The third paper shall be on the melting of steel, and the fourth on the uses of crucible steel received.

NOTE ON THE

ESTIMATION OF GOLD, TIN, AND CADMIUM IN ALLOYS.

By WILLIAM FRENCH, B.A., A.I.C.

DURING last autumn I had occasion to analyse some alloys containing gold, tin, and cadmium, and the method employed for separating the tin from the cadmium was that prepared by Löwenthal, viz., oxidising the solution of stannous chloride, and then warming up with a mixture of sodium sulphate and ammonium nitrate.

The oxide of tin frequently came down as a colloidal precipitate, which was extremely difficult to wash and collect, and the analyses required many hours for their completion. The filtrate from the oxide of tin was precipitated by sulphuretted hydrogen, and the cadmium sulphide washed to free it from ammonium and sodium salts, then dissolved in hot dilute hydrochloric acid. After filtering, the cadmium chloride was precipitated at the boiling-point with sodium carbonate; the cadmium carbonate filtered off and weighed as oxide in the usual manner.

As this method was tedious and lengthy I was led to try if other reagents could be used in place of ammonium nitrate, &c., and I find such a reagent in hydrogen peroxide which I have not yet seen anywhere described. My method consists essentially in adding hydrogen peroxide to a nearly neutral solution of the mixed chlorides of tin and cadmium, and warming. This precipitates the tin in a flocculent form, which readily settles and is capable of being filtered and washed with ease. The cadmium can then be precipitated direct from the filtrate with sodium or potassium carbonate.

A description of the analysis will make the above general statement clear. From one to two grms. of the alloy was heated with hydrochloric acid, using as little acid as possible to get the tin and cadmium into solution. The gold was next filtered off and weighed. To separate the tin from the cadmium, the filtrate was very nearly neutralised with potash, and from 4 to 5 c.c. of hydrogen peroxide (10 volumes) added; the whole, diluted to about half a litre with water, was then heated to the boiling-point. This throws down the tin in a very convenient form for filtering and washing; the precipitate after washing was dried, ignited, and weighed as SnO₂. The filtrate from the tin and washings were next evaporated to about half, and the cadmium precipitated at the boiling-point with potassium carbonate.

[This method gives good results with a mixture of tin and cadmium in solution, and also with the alloys I have tried is quite comparable with the other method, having the special advantage of a saving of at least half the time. Through the kindness of Messrs. Haycock and Neville I have been able to analyse some of their alloys, and here

give the analyses of two as compared with their analyses by the method mentioned by them (C. J. S., lix., 936) :—

Messrs. H. and N.	Modification.
(a). Au = 3.51 per cent.	3.68 per cent.
Cd = 9.86 "	10.13 "
Sn = 86.31 "	86.19 "
(b). Au = 29.16 per cent.	29.29 per cent.
Cd = 13.83 "	13.91 "
Sn = 56.67 "	56.82 "

Considering the method of preparation and object for which these alloys were made, it would be difficult to expect analyses to give more coincident results.

I am still studying the action of hydrogen peroxide as a means of separating tin from other metals.

University Chemical Laboratory,
Cambridge.

NOTE ON THE ANALYSIS OF SODIUM NITRITE.

By GEORGE LUNGE.

IN the CHEMICAL NEWS, vol. lxx., No. 1684, p. 100, Messrs. Green and Evershed object to my method for estimating nitrous acid in sodium nitrite (which they otherwise acknowledge to be correct) as not giving accurate results in the presence of organic matter or other reducing substances. Since, however, as everybody knows, sodium nitrite is manufactured by fusing sodium nitrate with lead or copper, it would seem to be really very superfluous to take any account of organic matter or any other reducing substances in the present case. My method has been quite recently submitted to a totally independent examination by Professor Stutzer, of Bonn, and Dr. Reitmaier (*Zeitsch. für Angew. Chemie*, 1891, Part 22), who came to the conclusion that it is both easy of execution and perfectly correct.

Messrs. Green and Evershed prefer a method which they have published in 1886, and of which they believe they have been the first inventors. About eight years before their publication, however, I became acquainted with the identical method for testing nitrites, as being then in current use at several German colour works. I must point out that aniline hydrochloride was always employed then, not sulphanilic acid. I tried that method for myself, but rejected it as far more troublesome and far less accurate than the permanganate method. I remember perfectly well, when Messrs. Green and Evershed's paper came out, showing it to my demonstrator and remarking that their method lacked both novelty and usefulness. It is a mistake to say that I quote Baeckmann as the author of that method; I only quoted his handbook of technical analysis as my source for the description of the aniline method, as practised by the colour works' chemists, which description, by the way, is really identical with Messrs. Green and Evershed's way of proceeding (working with aniline and hydrochloric acid in an ice-cooled vessel, and testing by drops on iodised starch).

Apart from being decidedly inaccurate, the aniline method (letting alone sulphanilic acid) is at the best a tedious and troublesome process according to Messrs. Green and Evershed's own showing. You must start with absolutely pure dry anilines; you must work in a vessel cooled by ice; you must wait a few minutes after each addition of the nitrite solution, and a full hour after the last addition in order to see whether the reaction for nitrous acid does not vanish again.

You must take account only of a colour produced at once with the starch solution, as, on standing, the drop nearly always becomes blue. It is evident that sources of error are lurking all over here. Even Messrs. Green and Evershed themselves, who have probably more practice with

their method than most other people, do not profess to have come nearer the true result, as indicated by Kinnicutt's method, than 0.4 per cent; but in the numerous tests made by myself and my students with the aniline method both before and after the appearance of their paper, we have not obtained anything like such good results.

I could not but come to the conclusion that both the aniline and sulphanilic acid methods, which have led to many disputes between buyers and sellers, must be rejected as misleading, whilst the permanganate method as modified by me gives absolutely uniform and correct results, with the very great advantage of each test requiring only a few minutes and being accurate even in less skilful hands. It is no matter of surprise that my method seems to have met with approval by the leading Continental manufacturers and buyers of nitrite of soda.

THE FERMENT OF THE OPIUM OF SMOKERS, AND ITS ARTIFICIAL FERMENTATION.

THE smokers' opium, cleared of the rank and empyreumatic principles which this product contains in the raw state, cannot be offered for sale by the Régie until it has been subjected to a spontaneous fermentation, the duration of which is not less than ten to twelve months.

Chemical analysis has always been powerless to grasp the modifications which this fermentation causes, on account of their very complicated nature. We merely know that, in order to be consumable, the complete chandoo must be beaten in the air, then left in large vats for a long time. Its surface becomes covered little by little with a crust of moulds, which in some places swells, and in others sinks, grows wrinkled and dry. The opium has then acquired a kind of bouquet more or less delicate, which is appreciated by the smoker, and, in particular, it has lost the rank odour and acrid taste of burnt horn which characterise newly made opiums. Finally, the kneading of the paste becomes more easy, and the pipe is smoked without further delay.

M. Lalande, who, in 1890, published in the *Archives de Médecine Navale et Coloniale* a very complete account of the opium of smokers from a chemical point of view (which study was analysed in the *Revue* of August 16, 1890, p. 220), very judiciously ascribes this fermentation to aerial microbia; but he found it impossible to study the development of these microbia; he was merely able to observe that they existed, and he mentioned the scientific interest which a deeper study of the question might present.

The reading of this work suggested to M. Calmette the idea of utilising the resources of the Laboratory of Microbiology, at Saigon, for the purpose of solving the problem posed by M. Lalande.

It was, in fact, apparent that it would be of great practical utility to endeavour to find methods for producing artificially the fermentation of opiums; as in industry they cause fermentation with beer barm in brewery malt. If this idea became feasible it would then be possible to obtain chandoos already fermented and fit for consumption in a relatively short time; one or two months, for example, instead of ten or twelve months; and the Custom House and Régies would thus immediately have at their command a capital of 1,500,000 francs, represented by the chandoo in course of spontaneous fermentation.

Besides this unproductive capital, the colony is not only exposed to the risk of fire and theft, but undergoes also, through slow evaporation of the opiums, a dead loss of some considerable extent, which rapid fermentation could avoid.

This is the method followed by M. Calmette as it is

described in the *Archives de Médecine Navale et Coloniale*, Feb., 1892:—

In artificial bouillons prepared with rinds of opium balls and heated at 120°, so as to destroy all foreign germs other than those he wished to sow, M. Calmette successfully isolated in the different opiums, in fermentation of various ages, a large number of microscopic vegetables belonging to the class of myzomycetes or lower order of fungi.

Bacteria, properly so called, are almost entirely absent in chandoos of good quality. We only find in some vats colonies of the *Bacillus subtilis*, a very common microbe in nature, and which thrives in most vegetable infusions. This microbe grows under the form of a wrinkled veil on the surface of the fats, depriving the sub-adjacent opium of the amount of air necessary for its normal fermentation in such a way that this last cannot take place until much later, when the *Bacillus subtilis* dies, having exhausted all the elements it could monopolise for its nutrition. It is then a question here of an opium parasite; a bad ferment which must be eliminated.

The best opiums are given by vats in which M. Calmette exclusively found *Aspergillus* and *Mucors*; the last much less numerous than the first. The *Aspergillus* belong to several species, but the most common are the *glaucus* and *niger*. In very old opium, considered as the best of the Régie, the author found perfectly pure cultures of the *Aspergillus-niger*. It was then already indicated to try the artificial culture of this organism on new chandoo.

The *Aspergillus niger* easily grows in all acid mediums containing mineral elements in sufficient proportion, and its spores abound in the air of all hot or temperate climates. Its methodical culture based on the analysis of its peculiar chemical constitution was realised in France by M. Raulin, who for this object composed a very complicated liquid in which this microscopic vegetable grows with great rapidity and vigour.

This artificial liquid, employed by M. Calmette, is composed as follows:—

	Grms.
Water	1500
Sugar candy	70
Tartaric acid.. .. .	4
Nitrate of ammonia	4
Phosphate of ammonia	0'60
Carbonate of potash	0'60
" magnesia	0'40
Sulphate of ammonia	0'25
" iron	0'07
" zinc	0'07
Silicate of potash.. .. .	0'07

If any of these eleven elements are suppressed, or the proportion limited, the culture of the vegetable falls off, and the weight of the plant furnished in the same time is much less. On this medium, in four days the liquid surface is entirely covered with a felted ramified mycelium supporting a multitude of small cylindric columns, on which are implanted black spherules with spores. These last, transported on the opium, easily germinate and run over all its surface, forming a velvety crust wrinkled over all its extent.

It is then very easy to cultivate the *Aspergillus* on the Raulin liquid; in the first place, to obtain the quantity of sowing required and with the spores obtained it only remains to sow the surface of the chandoo, which is to be put into a state of fermentation. Only, to obtain a rapid development* of the vegetable, it will be necessary to operate in very wide flat vessels into which the air can easily enter. The thinner the layer of opium with regard to the surface, the more rapid will be the fermentation. Finally, the previous beating in the air, as practised by the Chinese empirically, has its reason of existence, because it multiplies the surfaces of the sowing, and also because it supplies the growing plant with a large amount of oxygen, very favourable to its growth.

The *Aspergillus* changes in a complex manner the composition of the chandoo at the various stages of its development. M. Calmette was able to observe its effects by syphoning under a layer of *lap lante* and, at various ages, the Raulin liquid, which he then replaced by other liquids containing, instead of sugar, dextrin or tannin.

We already knew that the *Aspergillus* secretes an inverting diastase, which at once transforms the sugar into glucose. The glucose is then burnt, and its last state is oxalic acid; dextrin undergoes the same change. M. Calmette was also able to observe that, if fresh, chandros sometimes contain more than 6 per cent of glucose, opium in which fermentation has ended only contains traces, which can hardly be perceived with the Fehling liquid or the polarimeter. The dextrin has completely disappeared. The tannin is entirely changed into gallic acid by the adult *Aspergillus*, but this transformation only occurs during sporulation of the plant. It is here a question of a division produced by the hydration of the tannin under the action of the diastases of the *Aspergillus*. M. Calmette found that in a porcelain basin covered with a plate of glass, ten days of fermentation were sufficient to take away all the tannin of a solution of 20 grms. per 300.

As for oxalic acid, produced by the combustion of the glucose and dextrin, it is again met with in the meshes of the mycelium in the form of oxalate of lime. The felted layer of the *Aspergillus* imprisons a multitude of microscopic crystals of this salt, of which the form is like that of an envelope for letters.

It does not appear either that the alkaloids are changed in their proportions by the development of the vegetable.

From a practical and even industrial point of view, perfect fixity of the quantities of alkaloids is only of minor importance. It is of little consequence to the smoker, in fact, whether the opium of the Régie contains 6 or 8 per cent of morphia; with about 2 grms. per cent he does not experience any difference in the effects on his organism. On the contrary, he can quite appreciate a pleasing flavour and sweet perfume in the opium, its burning well, its not igniting and drying too much in swelling. These qualities opium only acquires by fermentation, as it does not possess them at the time of its leaving the distillery.

The chief thing for the Régie is to obtain, as soon as possible, a completely fermented chandoo, and the laboratory experiments undertaken by M. Calmette demonstrate that this result can be attained in a maximum delay of one month. At the end of this time, the diastases of the *Aspergillus* have given their useful effect, the glucose and dextrin contained in the chandoo are destroyed, and the tannin transformed into gallic acid. Opium is then fit for consumption, and the tastings submitted to smokers' experts gave as result that the product of artificial fermentation has the qualities of old opium already some years of age; qualities which are much prized by the Chinese.—*Revue Scientifique*, Feb. 27, 1892.

ALUMINIUM SULPHIDE.

By H. N. WARREN, Research Analyst.

THIS compound, the production of which according to the numerous authorities upon the subject is brought about by the action of sulphide of carbon upon Al_2O_3 at a red heat, is said to possess a glassy appearance, to be fusible at a red heat, and instantly decomposed by water. Following up these statements and requiring this substance for further investigation the author has taken pure Al_2O_3 , prepared by dissolving the metal in HCl , evaporating to dryness, and calcining the same; this was subjected for about twenty minutes to the action of CS_2 aided by a full red heat; upon cooling, and withdrawing the same from its porcelain enclosure, the alumina remained unaltered.

even retaining its usual whiteness. This I was not surprised to discover, for future experience with this compound had led me to believe that alumina and also carbon disulphide were far more stable substances than these plausible theorists assert. Nothing daunted, however, I determined to give the trial every advantage, and urged the heat to whiteness for a full hour, meanwhile maintaining a rapid stream of gaseous carbon disulphide. Upon cooling and examining the contents, I soon discovered that I had to deal again with pure Al_2O_3 . Amongst various other suggestions I was led to consider the difficulties of producing pure alumina when precipitated from a solution of alum. Having procured a solution of potash alum, I precipitated the alumina contained therein by the addition of an excess of ammonia, washing the precipitate until free from sulphates, drying the hydrate thus obtained, and calcining to Al_2O_3 , with repetition of the former process.

Upon re-examining I now discovered the glassy melted mass which had been formed, which presented a strong odour of SH_2 when thrown into water. Upon more careful examination I discovered that after all I had only formed, instead of aluminium sulphide, a very small quantity of potassium sulphide, which my alumina had mechanically carried down as sulphate; but which, owing to the high temperature the whole had been subjected to, had naturally induced partial fusion. Is this the aluminium sulphide described by Fownes, revised by Gmelin, and most other supposed authorities? I am inclined to believe that it is as plausible as treating a mixture of $\text{Al}_2\text{O}_3 + \text{Cu} + \text{C}$ in order to obtain aluminium bronze (Watts's "Dictionary of Chemistry"), which experiment, when subjected to the oxyhydrogen furnace, resulted in pure copper (perhaps electricity would favour it a little).

Several other such results could be quickly enumerated, but the foregoing will perhaps be sufficient to encourage scepticism. To prepare aluminium sulphide subject aluminium at a red heat to the action of sulphur vapour.

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18, Albion Street, Everton, Liverpool.

ACTION OF NITRIC ACID ON ASPHALT AND CELLULOSE.

By REGINALD A. FESSENDEN.

IN view of the experiments of Luzi and Friswell on the action of nitric acid on graphite and coal, the following account of two substances which I prepared for commercial purposes may be of interest:—

Some years ago, in consequence of certain patent litigation, Mr. Edison requested me to find some non-fibrous substance suitable for lamp filaments which should have the same or greater efficiency than those made of bamboo. A great variety of new substances was prepared, and two of these seem worth description. Asphalt was taken and dissolved in chloroform. It was then treated with dilute nitric acid and the whole heated; the chloroform was then distilled off. The substance produced was dissolved in the chloroform and treated once more with stronger acid, and the chloroform was then distilled off again.

The residue was a light brown substance if the acid had been of a proper degree of dilution. If the acid had been too strong, the substance was of a shiny black colour, due to the formation of a secondary product. This secondary product is soluble in alcohol, and may be separated by dissolving the substance left after the distillation in chloroform and then adding alcohol. The light brown substance is then precipitated in a pure state. This latter when heated chars without swelling or puffing, and turns to a very hard dense charcoal. If any traces of the black substance are left, it puffs up very much. The black substance seems to be a compound containing nitrogen.

The brown substance is insoluble in most of the ordinary solvents, but is dissolved by chloroform and a few of the essential oils, such as oil of birch. On being triturated with chloralhydrate, the mixture turns to a thick liquid. In manufacturing the filaments, a thick paste of the light brown substance and chloralhydrate was squirted through a dye into filaments, which on being carbonised at a very high temperature shrunk considerably, and made a filament much more durable and economical than any hitherto produced. The filament was so elastic that it could be tied into a knot of $\frac{1}{8}$ of an inch diameter, and was strong enough to penetrate the skin like a needle.

The second substance was formed by treating cellulose with dilute nitric acid, thereby forming the oxy-cellulose of Messrs. Cross and Bevan. This oxy-cellulose is soluble, on digestion, in ammonia, and on evaporating the solution a transparent film is left, which by its odour when burnt seems to be nitrogen compound of cellulose; it very strongly resembles gelatin in appearance, flexibility, and odour when burnt, and might, on account of its solubility in ammonia, be of use for photographic plates.

On account of the pressure of work at the time no analysis was made of either of these compounds.

THE SEPARATION OF BISMUTH AND CADMIUM.

By PAUL JANNASCH and P. ETZ.

IN the separation of certain metals of the sulphuretted hydrogen group, such as lead, bismuth, cadmium, and tin, according to the customary methods, we not seldom encounter unexpected difficulties which seriously affect the accuracy of the results. More trustworthy are evidently separations in a current of chlorine, most of which have already been studied.

The decided advantages which bromine permits of in its use, as well as my observation that the temperatures of volatilisation of the metallic bromides differ more widely among themselves than those of the corresponding chlorides, induced me to re-examine the analyses which I effected some years ago with bromine-vapour, and to extend the method. The first investigation of this kind, undertaken in concert with Herr P. Etz, fell out so favourably that we could hope by means of our new process to enrich quantitative analysis with a series of exceedingly simple and accurate metallic separations.

Our procedure was the following:—As initial material, we used cadmium sulphate and metallic bismuth, of the purity of which we satisfied ourselves by especial analyses. These substances were dissolved in nitric acid, the solution evaporated down on the water-bath, and the residue taken up with as much hydrochloric acid as was necessary to prevent the deposition of basic bismuth chloride on the addition of about 100 c.c. of water. From this solution, which was heated to ebullition, the metals were thrown down as sulphides by means of a current of sulphuretted hydrogen, collected upon a filter, dried, and weighed at 100° , washed with hot sulphuretted hydrogen water, and then completely dried in an air-bath and weighed.

The desiccated mixture of sulphides was placed in a porcelain boat in a dried tube of potash-glass, and a brisk current of air, which had traversed a cylinder containing bromine, was passed over it from a gasometer. The bromine acts upon the substance even in the cold, but the reaction must be assisted and completed by moderate heating with a gas flame $1\frac{1}{2}$ inches in height kept in a wavering motion, during which we may observe in the tube the occasional appearance of a russet-yellow flame.

After about half an hour, all the bismuth has been carried into the receivers, which have been charged with weak hydrochloric acid, whilst all the cadmium remains behind in the boat as a bromide. This bromide is dis-

solved in a little dilute hydrochloric acid, heated to ebullition, and precipitated with sodium carbonate. The solution of bismuth taken from the receivers was evaporated down, and this operation was repeated two or three times after adding nitric acid, in order to eliminate the hydrochloric acid, which would interfere with the subsequent precipitation. In their future operations the authors will fill the receivers with very dilute nitric acid instead of hydrochloric acid. The bismuth is finally separated by boiling with a mixture of ordinary ammonium carbonate and a little ammonia.

The complete separation of the bismuth appeared on the careful examination of cadmium. No trace of a brown precipitate appeared on passing sulphuretted hydrogen into the hydrochloric solution. The precipitate was a pure yellow from the first. Moreover, the solution of cadmium, copiously diluted with water, gave no milky turbidity of bismuth oxychloride.

The mixed sulphides must be perfectly free from water when exposed to the action of the current of vapour of bromine. — *Berichte der Deutsch. Chem. Gesell.*, xxiv. p. 3746.

THE SEPARATION OF BISMUTH AND LEAD.

By P. JANNASCH and P. ETZ.

AFTER obtaining so favourable results with the separation of bismuth and cadmium in a current of bromine vapour and air, we endeavoured in the same manner to effect a trustworthy quantitative separation of bismuth and lead. The fact was confirmed that the products of volatilisation of the metallic bromides lie relatively more remote from each other (as regards the temperature of volatilisation) than the corresponding chlorides. Hence there is no difficulty in volatilising bismuth in presence of lead by merely heating their sulphides in a current of bromiferous air with a gas-flame $1\frac{1}{2}$ inches in height.

In the execution of our method metallic bismuth and pure lead nitrate were dissolved in pure nitric acid, the metallic salts were evaporated to dryness, again taken up with water, and the necessary quantity of hydrochloric acid, the rather dilute solution is precipitated whilst hot with sulphuretted hydrogen, the precipitated sulphides are dried at 100° , placed in a porcelain boat which has been previously weighed, and heated in a current of air and bromine vapour. Bismuth bromide distils over completely, whilst lead bromide remains in the boat in a state sufficiently pure for weighing. The receivers for the bismuth bromide contained very dilute nitric acid.

For success the following precautions are absolutely necessary. The sulphides obtained must not be allowed to stand a long time, either in the liquid or in the funnel, &c., but the operation must be proceeded with as soon as possible. We have observed that a too prolonged action of the air upon the mixed sulphides is decidedly injurious and sometimes may lead to results which are completely worthless. Such preparations when subsequently heated in the current of bromine vapour do not yield simply pure bromides, but simultaneously basic compounds,—a circumstance which more or less interferes with the complete volatilisation of the bismuth. We therefore made the following arrangement. In the evening the solution was placed ready for the introduction of the sulphuretted hydrogen, so that the precipitation may be effected without loss of time the next morning. The filter is carefully lifted out of the funnel and dried, first on a flat porcelain capsule, and then in the funnel, so that in the afternoon, after the commencement of the analysis, we were able to undertake the heating in a current of bromine vapour. The expulsion of the bismuth by bromine succeeded best when a somewhat abundant quantity of sulphur was mixed with the precipitated sulphides. Hence it is advantageous to add to the hydrochloric solution of the metals a few

drops of red, fuming nitric acid, prior to the introduction of the current of sulphuretted hydrogen.

The mixed sulphides in the porcelain boat, before their introduction into the glass tube, should be duly comminuted by means of a platinum rod, in order, on the one hand, to admit of a rapid and thorough-going action of the bromine, and on the other to prevent the projection of particles, which is apt to occur if the mass consists of large fragments.

The current of bromine from the very commencement of the operation should be rather rapid (about 300 gas bubbles per minute from a glass tube of 6 m.m. in width, since a deficiency of bromine may interfere with the formation of the volatile bismuth tribromide, and may also allow of sublimation in the wrong direction. At the end of the operation, and whilst the tube is cooling, the current may be moderated accordingly.

As it is found disadvantageous to leave the mixed sulphides in the drying-closet at 100° too long, it is better to put an end to the desiccation as soon as the loss of weight of the substance does not exceed a few m.grms. in a quarter of an hour. Hence it appears necessary before commencing the bromine treatment to pass first a current of dry air over the substance in the boat at a very gentle heat, so that the moisture still present may be carried over into the receiver.

In the treatment with bromine an unnecessarily strong heat must be avoided. A Bunsen flame of 8 c.m. in height is sufficient. The tube is first heated in front of the boat, waving the flame to and fro, and then the boat itself is gradually heated until the residual lead bromide melts. When all the bismuth has been driven as far forward as possible the flame is brought back to the boat, its contents being again heated to fusion. This is repeated two or three times, and when nothing further passes over, the heat must not be increased, but the contents of the tube are allowed to cool quietly in the current of bromine.

The lead is weighed first as bromide in the boat and finally as sulphate, into which state it is converted by heating the bromide with saturated chlorine water and precipitating the solution of lead chloride with sulphuric acid.

The solution of bismuth nitrate in the receivers is concentrated, precipitated at the temperature of ebullition with ammonium carbonate, and weighed as bismuth oxide. The ignited oxide is covered with solution of ammonium carbonate, evaporated on the water-bath, heated more strongly in an air-bath, and fully ignited to expel any traces of sulphuric acid. — *Berichte der Deutsch. Chem. Gesell.*, vol. xxv., p. 124.

ON A SERIES OF NEW COMPOUNDS— CHROMOSULPHURIC ACID AND THE METALLIC CHROMOSULPHATES.

By A. RECOURA.

IN a recent memoir I described the preparation and the properties of a compound isomeric with chromium sesquisulphate, Cr_3SO_4 , which I named provisionally green chromium sulphate, although it neither presents the characters of a sulphate nor those of a salt of chrome. I have shown, in fact, that this compound does not admit of double decompositions; thus its solution does not precipitate barium chloride as do all the sulphates. Hence I concluded that this compound is not a salt, but a compound of a peculiar nature.

I purpose demonstrating in this paper that a mol. of this compound may combine with a mol. of sulphuric acid or of any metallic sulphate, forming compounds such as $\text{Cr}_3\text{SO}_4 \cdot \text{SO}_4\text{H}_4$ or $\text{Cr}_3\text{SO}_4 \cdot \text{SO}_4\text{K}_2$, or, again, $\text{Cr}_3\text{SO}_4 \cdot \text{SO}_4\text{Zn}$, &c.,—compounds in which all the sulphuric acid is masked, that of the metallic sulphate as

well as that of the chromium compound; whilst, on the contrary, the metals K, Zn, &c., may be shown by the ordinary reagents, so that we may consider these compounds, which are neither sulphates nor salts of chrome, as salts of a peculiar acid $(Cr_24SO_4)_H_2$, an acid having a complex radicle like the chromocyanhydric acid, and which I call chromosulphuric acid.

The fundamental experiment which establishes the existence of these compounds is the following:—We mix a solution containing 1 mol. of the compound (Cr_23SO_4) with a solution containing 1 mol. of sulphuric acid or of any metallic sulphate whatever, e.g., a mol. of copper sulphate. Combination takes place immediately; for if we pour barium chloride into the liquid thus obtained we observe no precipitate. The liquid therefore contains no sulphate, the sulphuric acid of the sulphate being entirely involved in the chromic radicle. The liquid no longer presents the reactions of a chromic salt, though it yields those of the salts of copper; it is therefore a solution of copper chromosulphate, $(Cr_24SO_4)Cu$.

The radicle of these salts is unstable, that is, only in the dissolved chromosulphates. After the lapse of half an hour or sometimes less, according to the nature of the compound, the solution begins to be precipitable by barium chloride; it is precipitated immediately if heated to ebullition. To observe the absence of the production of barium sulphate it is necessary to operate only with very dilute solutions, otherwise the chromic radicle is decomposed and a precipitate is formed.

The following are the methods of preparing these salts in the solid state and their properties:—

Chromosulphuric acid, $(Cr_24SO_4)_H_2, 11H_2O$.—To obtain this compound in the solid state I reduce chromic acid with alcohol in presence of a suitable quantity of sulphuric acid and the smallest possible quantity of water. As this process is delicate I will describe it in detail. I mix 50 grms. of chromic acid with 25 grms. of water and 50 c.c. of concentrated sulphuric acid. I pour into this mixture drop by drop 15 c.c. of alcohol at 95 per cent, taking care that the temperature does not rise above 30°. I thus obtain a green syrup, which is drained to separate it from unreduced chromic acid; it is then ground up in a mortar with an equal volume of crystallisable acetic acid. This precipitates the chromic acid from its solution, and there is obtained a green paste which is rapidly drained on the Sprengel pump to separate the acetic acid. The compound is then left in a vacuum until it is inodorous.

We obtain thus a green powder, $(Cr_24SO_4)_H_2, 11H_2O$. This is chromosulphuric acid, which is very hygroscopic and deliquesces rapidly in moist air. But in dry air it may be preserved indefinitely; its solution is very unstable. This instability is due on the one hand to its slight formation heat, and on the other to the instability of the compound Cr_23SO_4 , which as soon as formed begins to transform itself into the violet chrome sulphate. This instability of chromosulphuric acid in solution is manifested in various ways. In the first place the solution, which is at first of a fine green, turns by degrees to blue. After some days it is merely a mixture of violet chrome sulphate and of sulphuric acid.

Potassium Chromosulphate, $Cr_24SO_4K_24H_2O$.—In order to obtain this compound in the solid state we must not attempt to crystallise its solution. The most simple method is to partially dehydrate by heat chrome-alum. This compound is kept for some hours at 90°, when it loses 12 mols. of water. It is then kept at 110° until it only contains 4 mols. of water. We thus obtain a green powder, which is potassium chromosulphate. Sodium chromosulphate, $[Cr_24SO_4]Na_210H_2O$, is prepared similarly to the potassium salt.

Ammonium chromosulphate, $[Cr_24SO_4](NH_4)25H_2O$, is prepared like the former. It is a pale green powder which dissolves in water in a few minutes. The alkaline chromosulphates are prepared also by a second method, which consists in reducing a mixture of bichromate and sulphuric acid and sulphuric acid with alcohol as in

preparing chrome-alum, but in presence of a very small quantity of water.—*Comptes Rendus*, vol. cxiv., p. 477.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 3rd, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

MESSRS. G. P. Darnell Smith, Ernest J. Parry, Robert Ludwig Mond, W. P. Hatton, and W. J. A. Butterfield were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Price Dodds, 3, Eversley Place, Heaton, Newcastle-on-Tyne; Henry Ellison, Whitechapel Road, Cleckheaton; Albert Augustus Lintern, High School, Middlesbrough; Herbert Edward Lindley, 13, St. Bartholomew Road, Camden Road, N.; John Northing, 96, Tretonville Road, Sandymount, Co. Dublin; Frederick J. Oldershaw, 34, Bramhall Lane, Stockport; Albert Ernest Richardson, 4, Black Hall Road, Oxford; James Stenhouse, Tanfield, Inverleith Row, Edinburgh.

Address to Professor Bunsen.

It was announced that it was proposed to present an Address to Prof. Bunsen, who has now been fifty years a Foreign Member of the Society, and that among those who sign it all those who have been his pupils should, as far as possible, be included. (See p. 121).

Of the following papers, those marked * were read:—

*112. "A Rule for Determining whether a Given Benzene Mono-derivative shall give a Meta-di-derivative or a Mixture of Ortho- and Para-di-derivatives." By Professor CRUM BROWN and Dr. GIBSON.

The rule suggested will be understood after reference to the accompanying table (see next page).

It will be seen that whenever the *hydride* of the radicle (column C) contained in the mono-derivative (column A) is asterisked, column E shows that a mixture of ortho- and para-di-derivatives is formed, and that whenever the *hydroxide* of the radicle (column D) contained in the mono-derivative (column A) is asterisked, column E shows that the meta-derivative is obtained.

The substances marked with an asterisk in column C are such hydrides as are *not* convertible by *direct* oxidation into the corresponding hydroxides in the next column whereas those asterisked in column D are compounds which can be formed by *direct* oxidation from the corresponding hydrides; the rule is based on this distinction.

DISCUSSION.

Mr. GROVES having referred to the statement which was on record that hydrogen chloride was oxidisable to hypochlorite by permanganate,

Prof. THORPE said that this was an error, and arose from the use of impure permanganate, made by the old-fashioned method with the aid of chlorate.

Dr. ARMSTRONG remarked that the rule suggested might be regarded as a modification of the usual statement that derivatives containing *acid* radicles gave meta-derivatives, since not only NO_2 , SO_3H , CO_2H , but also COH and COR , might be ranked as acid radicles. In neither form, however, did the rule apply to such a case as that afforded by dimethylaniline, which yield much meta-derivative.

*113. "The Relative Orienting Effect of Chlorine and Bromine. (I.) The Constitution of Parabrom- and Parachlor-Anilinesulphonic Acids." By HENRY E. ARMSTRONG and J. F. BRIGGS.

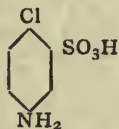
The case studied is that afforded by parachlorobromobenzene; it is found that when sulphonated this yields a uniform product characterised by a sulphochloride melt-

A.	B.	C.	D.	E.
C_6H_5Cl	$\cdot Cl$	HCl^*	$HOCl$	$o\text{-}p.$
C_6H_5Br	$\cdot Br$	HB^*	$HOBr$	$o\text{-}p.$
$C_6H_5CH_3$	$\cdot CH_3$	HCH_3^*	$HOCH_3$	$o\text{-}p.$
$C_6H_5NH_2$	$\cdot NH_2$	HNH_2^*	$HONH_2$	$o\text{-}p.$
C_6H_5OH	$\cdot OH$	HOH^*	$HO\cdot OH$	$o\text{-}p.$
$C_6H_5NO_2$	$\cdot NO_2$	HNO_2	$HO\cdot NO_2^*$	$m.$
$C_6H_5CCl_3$	$\cdot CCl_3$	$HCCl_3^*$	$HO\cdot CCl_3$	$o\text{-}p.$
$C_6H_5CO\cdot H$	$\cdot CO\cdot H$	$HCO\cdot H$	$HO\cdot CO\cdot H^*$	$m.$
$C_6H_5CO\cdot OH$	$\cdot CO\cdot OH$	$H\cdot CO\cdot OH$	$HO\cdot CO\cdot OH^*$	$m.$
$C_6H_5SO_2\cdot OH$	$\cdot SO_2\cdot OH$	$HSO_2\cdot OH$	$HO\cdot SO_2\cdot OH^*$	$m.$
$C_6H_5CO\cdot CH_3$	$\cdot CO\cdot CH_3$	$HCO\cdot OH_3$	$H\cdot CO\cdot CH_3^*$	$m.$
$C_6H_5CH_2\cdot CO\cdot OH$	$\cdot CH_2\cdot CO\cdot OH$	$H\cdot CH_2\cdot CO\cdot OH^*$	$HO\cdot CH_2\cdot CO\cdot OH^*$	$o\text{-}p.$

ing at 66° , which crystallises in massive, prismatic plates very similar to paradibromobenzene sulphochloride, the corresponding amide melting at about 178° (uncorr.).

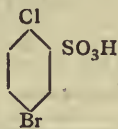
To determine the constitution of this product, the amido-acids prepared by sulphonating parabromaniline and parachloraniline were converted into chlorobromobenzenesulphonic acids; they gave isomeric acids, as should be the case if they were of corresponding constitution, the acid prepared from parachloranilinesulphonic acid being identical with the product from chlorobromobenzene.

According to Claus and Mann (*Annalen*, cclxv., 92), parachloraniline yields two isomeric acids on sulphonation, one being formed in but small quantity. The authors have been able to obtain only one acid; they have, indeed, observed that no fewer than three distinct forms of crystals separate from the aqueous solution of the product—long, striated rods springing from a common centre; rectangular, apparently rhombic prisms; and rhombs, probably monoclinic, which rapidly become opaque on exposure to air; but these appear to be all one substance, the difference in form being conditioned by difference in the amount of water of crystallisation. Claus has assigned the formula—



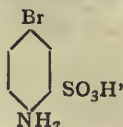
to the acid. This is confirmed by the authors, who find that, on displacing the NH_2 by hydrogen by the hydrazine method, the acid yields chlorobenzeneorthosulphonic acid.

Hence it follows that the acid formed by sulphonating parachlorobromobenzene is—



It would seem, therefore, that the chlorine rather than the bromine "attracts" the sulphonic group; but it will be necessary to ascertain whether the isomeric acid is not perhaps a less stable form, in which case it may be that the final product is not merely the product of direct sulphonation.

The chlorobromo-acid prepared from parabromaniline-sulphonic acid yields a sulphochloride crystallising in ill-defined plates melting at 46° , the corresponding amide melting at about 191° (uncorr.); the fact that it is different from the chlorobromo-acid prepared from parachloroaniline-sulphonic acid is in itself conclusive evidence that the acid obtained from parabromaniline is not—



as Borns asserts, but that it corresponds in constitution to the acid prepared from parachloraniline, as might indeed be expected to be the case. Borns (*Annalen*, clxxxvii., 372) bases his conclusion as to the constitution of the acid on its conversion by displacement of the NH_2 group by hydrogen into bromobenzenemetasulphonic acid, but no proof that he was dealing with this and not the ortho-acid is given beyond that contained in the bare statement that his product was recognised as the meta-acid from the composition and properties of the potassium and barium salts, the chloride (oily) and amide (m. p. 154°). The bromosulpho-acid obtained by the authors, however, yields an amide melting at about 183° , and is, undoubtedly, the ortho-acid. Parabromaniline-sulphonic acid crystallises in three distinct forms closely resembling those in which the parachloro-acid crystallises.

DISCUSSION.

The PRESIDENT remarked that it was usually supposed that NH_2 , like OH , had a powerful directing influence, and therefore it appeared remarkable that para-brom- and chlor-aniline should yield sulphonic acids in the formation of which this influence of the NH_2 group apparently did not come into play.

Dr. ARMSTRONG, in reply, said he thought it probable that in consequence of the formation of sulphate, the NH_2 group was rendered ineffective, and as the para-position is blocked by it, necessarily an ortho-chloro- or bromo-sulphonic acid was formed.

*114. "Note on Anhydrides of Sulphonic Acids." By HENRY E. ARMSTRONG.

Hitherto but little attention has been paid to this class of compounds: not long after Hübner, in 1884 (*Annalen*, ccxxiii., 238) had described a series of somewhat unsuccessful attempts to prepare phenylsulphonic anhydride, Abrahall succeeded in obtaining this compound by interaction of phenylsulphonic chloride and silver phenylsulphonate (*cf. C. S. Trans.*, 1886, 692); he describes it as crystallising from chloroform in fine prisms melting at 54° , and as being extremely deliquescent. Meanwhile it had been observed in Victor Meyer's laboratory that a number of bromo- and chloro-derivatives of thiophene, as well as paradibromobenzene and 1:2:4-tribromobenzene, gave sulphonic anhydrides directly on treatment with pyrosulphuric acid, all the anhydrides thus obtained being remarkable on account of their very slight solubility, even in boiling water, and the difficulty with which they were hydrolysed (*cf. Berichte*, 1886, 652).

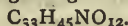
In the course of the experiments with parachlorobromobenzene, referred to in the previous abstract, it was noticed that whereas this was wholly converted into sulphonic acid by so-called 100 per cent acid, a fuming acid containing about 20 per cent of anhydride gave as chief product a microcrystalline anhydride similar to that prepared by Rosenberg from paradibromobenzene. On contrasting the behaviour of paradichloro-, chlorobromo-, and dibromo-benzenes with such fuming acid, it was found that the dichloro- gave relatively the smallest, and the dibromo-derivative the largest, yield of anhydride, monochlorobenzene yielding only sulphonic acid and sulphone. It therefore seemed probable that the anhydride was a

secondary product formed by dehydration of the sulphonic acid under the influence of the sulphuric anhydride: and that this is the case is shown by the fact that if, for example, potassium dibromobenzenesulphonate be mixed with fuming sulphuric acid, it is converted into the corresponding anhydride. To judge from a statement made by Bässmann (*Annalen*, xcxi., 213), it would seem that, in some cases, such anhydrides may be precipitable even from aqueous solutions of sulphonates. Obviously there are the same differences between sulphonic acids as between carboxylic acids with regard to the readiness with which they undergo dehydration.

*115. "Contributions to the Knowledge of the Aconite Alkaloids. Part II. The Alkaloids of true *Aconitum Napellus*." By Professor DUNSTAN and Mr. JOHN C. UMNEX.

The authors have examined the alkaloids of true *Aconitum napellus* plants grown by Mr. E. M. Holmes at the instance of the British Pharmaceutical Conference. The alkaloids were extracted from the roots by the following process, which precludes the possibility of the occurrence of hydrolysis, &c.:—The solution obtained by percolating with cold refluxed fusel oil (b. p. 100–132°) was agitated with water acidified with 1 per cent of sulphuric acid, and the resin having been removed by extracting the acid solution so obtained with chloroform, the liquid was made just alkaline with dilute ammonia and extracted with ether, which dissolved out a considerable quantity of alkaloid, but left in solution a further and smaller quantity, which was subsequently extracted by agitation with chloroform. The alkaloid soluble in ether was obtained as a gum-like mass incapable of crystallisation. By conversion into bromhydride it was separated into a crystallisable and an uncrystallisable salt.

The crystalline product was identified as the salt of aconitine, the crystalline and highly toxic alkaloid already described by one of the authors and Dr. W. H. Ince (*C. S. Trans.*, 1891). The alkaloid separated from the pure bromhydride melted at 188.5° (corr.), and afforded on combustion numbers agreeing with the formula—



The specific rotation of the bromhydride in aqueous solution was ascertained to be $[\alpha]_D -29.65$, a value which agrees with that previously recorded. As some doubt exists as to the solubility of aconitine in water, a determination was carefully made with this pure specimen. The mean of two determinations gave 1 grm. in 4431 grms. of water as the solubility at 22°; Jürgens had previously recorded the far greater solubility of 1 in 745 at the same temperature.

The non-crystalline bromhydride furnished a gummy alkaloid soluble in ether and alcohol, but only sparingly soluble in water, the aqueous solution being alkaline to litmus, and very bitter, but not giving rise to the tingling sensation so characteristic of aconitine. Not only the alkaloid, but also the chlorhydride, sulphate, nitrate, and aurichloride prepared from it could not be crystallised. This alkaloid is not identical either with aconine or with the picroaconitine of Wright and Luff. A full account of it will be given in a later paper, considerable progress having already been made in the most difficult task of isolating it in a pure state. The authors propose to assign to it the name *napelline*, which was first given to the alkaloid now known as pseudaconitine, and afterwards by Hübschmann to a substance which the work of Wright and Luff showed to be a mixture chiefly composed of aconine. The napelline obtained in the manner described is probably associated with another amorphous alkaloid about which they have at present little information to give beyond the fact that neither it nor its salts appear to crystallise.

The alkaloid soluble in chloroform was proved to be aconine, the compound which is obtained together with benzoic acid on hydrolysing aconitine.

The roots of true *Aconitum napellus*, therefore, must be

held to contain three alkaloids, one of which is crystalline, viz., aconitine, two being amorphous, viz., napelline and aconine. Indications have been obtained of the presence of a fourth alkaloid, which is amorphous and closely resembles napelline.

The authors find that the juice expressed from the roots contains a large proportion of amorphous bases but very little aconitine, the greater part of this latter remaining in the root, from which it may be extracted, together with the remainder of the amorphous alkaloids, by exhausting with amyl alcohol. The total quantity of amorphous alkaloid obtained amounted to more than twice that of aconitine.

The physiological action of the alkaloids referred to is being investigated. The results so far obtained point to the conclusion that crystalline aconitine is by far the most toxic alkaloid contained in *Aconitum napellus*.

(To be continued.)

INSTITUTE OF CHEMISTRY.

The Annual General Meeting was held at Burlington House on Tuesday, March 1, 1892, under the presidency of Dr. TILDEN, F.R.S. A strong muster of members was caused by the expectation of a lively meeting, it being known that opposition to the "house" list for the new council had been organised. The first business was the treasurer's report, which showed a large invested capital. The first "passage of arms" was initiated by Mr. C. T. KINGZETT, whose inquiry for the details of an item of £50 for "taking notes" of a conference in May last, but which were never issued to the members, was met by an emphatic refusal from Mr. DAVID HOWARD, the treasurer, and the PRESIDENT judiciously remarked that the account had been duly audited, that the council, and not the treasurer, was responsible, and that anybody could inspect the vouchers if he went to the offices of the Institute.

This over, the PRESIDENT referred to the labours of the retiring secretary, Mr. Charles E. Groves, F.R.S., and particularly to those of the last two years, and informed the meeting that the council had voted an honorarium of 100 guineas to Mr. Groves on his retirement. He also took this opportunity to introduce the new secretary, Mr. G. H. Robertson. Then came the President's Address, which was a vigorous defence of the professorial, as distinguished from the professional, element on the council. The "opposition" had made much of this preponderating influence; but its influence in numbers was reduced to actual facts very neatly by the Presidential remarks, whilst its influence as an "elevator" of professional efficiency was made much of.

The attempt at defining a professional chemist was dexterously put when Dr. TILDEN asked whether he was or was not the professor who trained and often gave advice in "consultation"; the "works" chemist, whose importance he magnified; or the analyst, who in luxurious reception-rooms gave advice, and who also did "water analyses" at 7s. 6d. a piece, or "carbon determination in steel" at 9d. a determination.

The PRESIDENT then feelingly referred to the losses by death of Drs. Heisch and Henry, F.R.S. Among others Dr. Tilden spoke of Thomas Hyde Hills as a warm friend. The address was spiritedly delivered, and even when assent was not given applause was accorded.

Dr. FRANKLAND, F.R.S., proposed a vote of thanks to the President, and asked that the Address should be printed, and, commenting on it, remarked that while infallibility could not be claimed for the council, honesty and a sincere desire to promote the interests of the profession could. He illustrated the absurdity of one section only predominating by a recital of what befell his spectacles years ago in Germany. The frame was made of silver, but gilt. The doctor then took them to a goldsmith for repair; this worthy declined to undertake the

matter as they were not all gold. Not disturbed, the doctor handed them to a silversmith; he, observing that they were not all silver, refused to repair them. So, inferred the speaker, you cannot have your Institute without alloy. Both elements were good, and to refuse to work together was folly indeed. Dr. Frankland instanced the legal profession, in which there was now a strong movement in favour of fusion of the two branches; also the medical, in which, although there was a certain amount of differentiation, yet there was a very considerable amount of unanimity.

Mr. WILLIAM THOMSON, of Manchester, the secretary of the association formed to promote united action among the opposition, supported Dr. Frankland's motion, and for himself and party disclaimed any intention or desire to attack the President or the Professor individually.

Mr. CASSALL, the opposition leader in the late council, also disclaimed, and professed his desire to keep the professors, but to get a more proportionate representation of the various classes of the profession. The motion was carried enthusiastically.

The report of the council was the next business, and after a small "wrangle" it was agreed to be taken "as read"; but remembering that the "closure" had been put upon further discussion on some previous occasion, the opposition, represented this time by Mr. Otto Hehner, the President of the Society of Public Analysts, moved to omit certain words in the report, and insert others, respecting the presentation of the scheme of examination for Fellows to the members before actual adoption.

Mr. HEHNER gave an important warning against stifling discussion, and urged that the Annual Meeting was the time, almost the only time, the members had of submitting their views to the council.

Mr. KINGZETT supported this view in trenchant terms. Mr. FRISWELL opposed it.

Dr. SMITH drew attention to the fact that the report was that of the council, and should either be received or rejected.

Seeing danger, Mr. TYRER reminded the President (who, by the way, had never been present at an Annual Meeting before) that one of his predecessors had ruled any amendment out of order, and, after the report had been accepted, ruled discussion thereupon, or upon questions relating to the policy of the council, also out of order; and concluded by asking the President whether he intended to adopt that unhappy precedent.

The PRESIDENT at once ruled that no amendment could be moved on the report of council, but gave the assurance that opportunity for free and full discussion should be given.

Scrutineers were next appointed, and voting proceeded. The names of nine censors nominated were put on the blackboard, and a ballot taken for four. The new secretary and Mr. Tyrer acted as counters. The censors are officers whose duty it is to investigate charges of unprofessional conduct of the part of the Fellows. Drs. Bell and Frankland and Prof. T. E. Thorpe came out highest, with Messrs. Cassall and Howard next with a tie, which the President untied, in accordance with the bye-laws, by giving a casting vote to Mr. Cassall, the opposition candidate,—a proceeding which brought down the house. The work of the scrutineers appeared likely to be lengthy, so a welcome adjournment for an hour and a half took place. In due time (nearly ten by the clock) the meeting resumed; but the results had leaked out beforehand, and there was considerable excitement as to what course the President would take. It must be first explained that many times during the evening had the legality of particular acts of the council and of persons been challenged, chiefly because of an ambiguity in the charter and the bye-laws in regard to "arrears." In the article of the charter relating to voting for the council it is specifically stated that no one in arrear on January 1, prior, &c., shall be eligible to vote; while immediately afterwards the word is used in relation to the rights of membership,

which cannot be taken away until the member has been twelve months in "arrear." It was well known that "arrears" had been tendered in the room, and the interest grew intense when Mr. THOMSON, one of the scrutineers, rose to state that by direction of the secretary, Mr. Groves, they had "set aside" unopened 150 voters' envelopes, on the ground that the subscriptions of these voters had not been paid. Mr. HEHNER used emphatic language. Mr. CASSALL implored the President to act, in the presence of grave doubt, on former precedents, viz., to disregard the arrears in the limited sense, and to view the right to vote in the broad sense of a member's privilege.

The PRESIDENT, who kept quite cool, ruled that he had no choice but to decide that no vote of a member in arrear could be admitted; but, since among the opened papers there were admittedly those of members who had paid since January 1, he would accept the proposal for an adjournment of the meeting to Friday, March 11, when the same scrutineers would revise the unopened envelopes, and then reject the votes of those whose subscriptions were not then received. The new secretary was instructed to notify every member of the Institute of the adjourned meeting, and each of the 150 in arrear of subscriptions to pay up.

The formal motion for adjournment was made, and Mr. HEHNER proposed, at 10.45 p.m., a vote of thanks to Dr. Tilden for his urbanity, courtesy, and tact, which was well deserved and we may say "earned."

Adjourned General Meeting.

At the adjourned Annual General Meeting held on Friday, March 11th, Mr. Markly, the solicitor who has acted for the Society, was present. Proceedings opened by the PRESIDENT reading the opinion of counsel, which had been obtained relative to the right of members to vote who had not paid their annual subscription. The opinion was to the effect that all members might sign and return a balloting list, but that any member who had not paid his subscription was not entitled to vote on any motion.

After some discussion as to whether marks or comments invalidated voting lists, the PRESIDENT ruled, after consultation with the solicitor, that only those papers were invalid which contained more than the proper number of names, or which for any other reason produced an ambiguity in the minds of the scrutineers as to the intention of the voter.

The scrutineers were now dismissed to complete the task left incomplete through the rejection of the 150 voting lists. On their return they announced that the official list was duly elected.

President—W. A. Tilden, D.Sc., F.R.S., &c.

Vice-Presidents—J. Bell, C.B., Ph.D., D.Sc., F.R.S., &c., M. Carteighe, F.C.S., E. Frankland, D.C.L., F.R.S., &c., Charles E. Groves, F.R.S., &c., W. Ramsay, Ph.D., F.R.S., &c., J. Emerson Reynolds, M.D., F.R.S.

Treasurer—David Howard, F.C.S.

Ordinary Members of Council—M. A. Adams, F.C.S., A. H. Allen, F.C.S., F. Clowes, D.Sc., F.C.S., A. Dupré, Ph.D., F.R.S., &c., R. J. Friswell, F.C.S., A. J. Greenaway, F.C.S., H. J. Helm, F.C.S., D. B. Hewitt, M.D., F.C.S., &c., J. F. Hogdes, M.D., F.C.S., J. Hughes, F.C.S., E. Kinch, F.C.S., G. H. Makins, F.C.S., R. Meldola, F.R.S., &c., O. Hehner, F.C.S., H. F. Morley, M.A., D.Sc., F.C.S., F. J. M. Page, B.Sc., F.C.S., &c., R. T. Plimpton, Ph.D., F.C.S., A. Smithells, B.Sc., F.C.S., J. C. Stevenson, M.P., F.C.S., C. O'Sullivan, F.C.S., F. L. Teed, D.Sc., F.C.S., J. Millar Thomson, F.C.S., W. Thorp, B.Sc., F.C.S., T. E. Thorpe, Ph.D., F.R.S., &c., T. Tyrer, F.C.S., E. W. Voelcker, Assoc.-R.S.M., C. R. A. Wright, D.Sc., F.R.S., &c.

The Presence of Mannite and Sorbite in the Fruits of the Cherry-Laurel.—Camile Vincent and Delachanal.—These two compounds are present in equal proportions in the fruits of the cherry laurel.—*Comptes Rendus*.

NOTICES OF BOOKS.

The Foundations of Chemistry. ("Grundlagen der Chemie.") By D. MENDELEEFF. Translated from the Russian by L. JAWEIN and A. THILLOT. St. Petersburg: Ricker.

WE have here the eighth and concluding issue of the German version of Prof. Mendeleeff's great work. It embraces the platinum metals, as also silver and gold.

No generalisations are appended; but, *à propos* of the researches of Stas on the atomic weight of silver, there is a critique of Prout's hypothesis, in which is reproduced an extract from the address delivered by the author before the Chemical Society of London, in 1889. To this oration we need the less refer as it is in the hands of every reader of the CHEMICAL NEWS.

Of the work as now completed, if we leave on one side its very pronounced hostility to the doctrine of elemental evolution, it is scarcely possible to speak too highly.

Zeitschrift für Anorganische Chemie. Vol. I., Part 1. Edited by GERHARD KRÜSS (of Munich). Hamburg and Leipzig: Leopold Voss.

THIS new journal, exclusively devoted to inorganic chemistry, makes its appearance in a manner which augurs well for its future success.

The principal papers in its first number are an investigation of phosphorous sulphide, by T. E. Thorpe and A. E. Tutton.

This compound is obtained on heating together phosphorous anhydride and sulphur in an atmosphere of carbon dioxide or nitrogen. The reaction sets in at 160°, and the mixture solidifies without any development of gas. The result is an addition product of the composition $P_4O_6S_2$. On sublimation *in vacuo* it is obtained in crystals. If the quantities of the ingredients employed are too large (exceeding 3 to 5 grms. phosphortrioxide), a violent explosion may ensue. The compound melts at 102°, and boils at 295°. It deliquesces in the air, giving off an odour of sulphuretted hydrogen. It is readily soluble in double its volume of carbon disulphide, from which it crystallises out unchanged.

"On the Double Acids of Septatomic Iodine," C. W. Blomstrand.—This comprehensive paper discusses the so-called double or complex acids, but it does not admit of useful abstraction.

"Action of Hydrogen Peroxide upon some Fluorides and Oxyfluorides," A. Piccini.—The author, on April 5th, 1891, submitted to the Accademia dei Lincei a memoir on the action of hydrogen peroxide upon normal potassium fluoxymolybdate, in which he described the compound $MoO_3F_2 \cdot 2KFH_2O$. He also described a compound which he obtained on treating potassium fluoxytungstate with hydrogen peroxide. He describes now rubidium and cesium fluoxypermoxybdates and a triammonium fluoxypermoxybdate.

"On some Ammoniacal Platinum Compounds," Oscar Carlgren and P. T. Cleve.—The authors have studied the behaviour of sulphurous acid upon platinum iodonitrate, and that of hydrogen peroxide upon the platodiamine salts.

"The Production of Tungstates Free from Molybdates," Carl Friedheim and Rich. Meyer.—The authors prepare a saturated solution of ordinary sodium tungstate in cold water, and add in the cold hydrochloric acid until the solution is feebly alkaline. The paratungstate which crystallises out is re-crystallised once, by which the proportion of molybdenum in the product is reduced by four-fifths. Half of the salt present is decomposed by hydrochloric acid and a little nitric acid in a boiling solution, and the fine yellow hydrated tungstic acid obtained is thoroughly washed with hot water. It is then well stirred up with water and added in the smallest possible

quantities to the boiling solution of the other half of the salt until a specimen is no longer precipitated by an addition of hydrochloric acid. After adding a little hydrochloric acid to the filtered solution, it is heated to ebullition and repeatedly precipitated by means of sulphuretted hydrogen; the filtrate is concentrated (when a little more sulphide separates out), the blue solution is oxidised with a few drops of bromine water, and neutralised with sodium hydroxide, when the pure paratungstate is obtained on crystallisation.

The presence of molybdenum in tungstic acid and the tungstates appears to have been hitherto overlooked and raises the question whether the atomic weight of tungstate has been accurately determined.

The list of chemists who co-operate in the new journal contains the most eminent names in inorganic chemistry in all countries in which science is diligently cultivated. The list of papers that have been sent in for the succeeding numbers is such that they will without doubt be eagerly anticipated.

Instructions for the Use of Hunter and Driffeld's Actinograph. (Patented). Entered at Stationers' Hall. London: Marion and Co.

THE instrument described in this pamphlet will probably be of great service to photographers; though whether its name has been happily selected is a question into which we need not enter. It is not, as a reader might possibly expect, an apparatus for taking an observation of the intensity of the light and recording the results. It seems, on the contrary, merely to supply data for calculating what the light ought to be. The authors admit that "many photographers would prefer an actinometer or direct means of measuring the light;" but they consider the actinograph preferable, because from it "the condition of the light may be ascertained at the precise moment of making the exposure;" whilst an actinometer "gives the condition of the light some time previously."

The instrument in question consists of four scales, expressing respectively the light, the lens, the exposure, and the speed of the plate. The amount of light is shown by a revolving scale for every day of the year, and for every hour of the day when it is photographically active. It is assumed that, apart from atmospheric influence, the amount of light is "merely a function of the sun's altitude. A short sliding scale is to take account of the greater or less transparency of the atmosphere. It is marked with the words "very light," "bright," "mean," "dull," and "very dull;" and we are told that "the exposure must be selected opposite that point which most nearly corresponds with the atmospheric conditions at the time of exposure. A "mean" light is defined as being when there is "just sufficient sun to cast a very faint shadow," and very dull is to indicate the duller light in which it would be at all reasonable to take a photograph.

Above this is a longer movable slide indicating the time in seconds from 0.05 to 60.

At the bottom is a slip marked with figures indicating the speed of plate.

The pamphlet contains very full instructions for the use of the instrument, accompanied with examples. It is remarked that each particular actinograph is adapted only for a certain range of latitude.

On Stereochemistry and the Laws of the Rotatory Power.—Ph. Guye.—A reply to two memoirs by M. Colson (*Comptes Rendus*, cxiv., pp. 175 and 417). If we do not admit the reality of the formulæ, such as CH_3COO and $COOCH_3$, it is not possible to constitute stereochemistry. The chemical notation does not exclude molecular combination. Nothing in the theories of Le Bel and Van 't Hoff permits us to affirm that their notation implies that all the derivatives of a dextrorotatory body must be dextrorotatory.—*Comptes Rendus*.

OBITUARY.

THE LATE DR. C. MEYMOTT TIDY.

SANITARY and forensic chemistry have sustained a heavy and unexpected blow by the death of Dr. C. M. Tidy, which took place on Tuesday, March 15. Upon sanitary questions, especially with reference to water supply and river pollution, the deceased chemist took a prominent position. Not only was his knowledge profound, but it was ready at command. He was unrivalled in seizing at once upon the salient points of any question, and in devising experiments to test the accuracy of the arguments and theories adduced, whether by colleagues or opponents. In addition to these qualifications, he possessed in an eminent degree the *uncommon* faculty known as "common sense." Hence, Government Departments, Parliamentary Committees, Law Courts, and Municipalities accorded to his evidence and his opinions an almost unlimited weight. His papers read before the Society of Arts and his lectures delivered to the students at Lincoln's Inn were exceedingly valuable. Here, as on all other occasions, he was distinguished for his adroitness in tearing to pieces unfounded theories and exposing the hollowness of sensational schemes for the water supply of the metropolis. In conjunction with Mr. Crookes and Prof. Odling he had carried on for years a searching inquiry into the quality of the London waters, and had done much to dispel the scare which had been industriously created concerning the quantity of impurities said to be swallowed yearly by the people of London in the shape of water.

Dr. Tidy's principal works, in addition to the reports on the London water supply elaborated in conjunction with Mr. Crookes and Prof. Odling, are his "Handbook of Modern Chemistry" (1878); "Handy Book of Forensic Medicine and Toxicology," 1877 (in conjunction with W. B. Woodman); "Legal Medicine," 1883.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The Annual Meeting of the Institute has come and gone, and although the "House List" has been elected as the new Council, the results of the polling show that I was mistaken when I supposed that the opposition had comparatively few sympathisers. When one makes a mistake it is one's duty frankly to own it.

If, as in the present case, about one-third of the members of the Institute range themselves under the banner of the dissatisfied, it seems only fair and just that the newly elected Council, which presumably represents the majority, should as soon as possible take steps to ascertain the causes of dissatisfaction, and the wants of the members at large. Although, in the ordinary nature of things, it is impossible that all the former can be removed or all the latter can be supplied, much can no doubt be done to improve the present state of affairs.

This contested election will probably do good if both sides agree to work heartily together for the common weal, but if the body of members becomes split up, divided into parties and factions, it will certainly retard our progress towards the attainment of the end which the founders of the Institute had in view, namely, that of raising our profession so that it may ultimately take rank with the learned professions.—I am, &c.,

CHARLES E. GROVES.

Guy's Hospital, March 14, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 9, February 29, 1892.

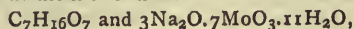
New Researches on the Monohaloidic and Monocyanic Aceto-acetic Ethers.—A. Haller and A. Held.—This paper is not suitable for useful abstraction.

Temperatures Developed in Industrial Furnaces.—H. Le Chatelier.—The author takes as points of comparison the melting-points determined by M. Violle, viz., sulphur 448°, gold 1045°, palladium 1500°, platinum 1775°. He finds the melting-heat of white cast-iron 1135°, and that of grey cast-iron 1220°. Mild steel melts at 1475°, semi-mild at 1455°, and hard steel at 1410°. The furnace for hard porcelain at the end of the baking has a heat of 1370°. The heat of a normal incandescence lamp is 1800°, but it may be pushed to beyond 2100°. Previous determinations have been falsified by using for comparison the melting-points of palladium and platinum. Thus the temperature of the Bessemer process was fixed by Langley at 2000°, because platinum seemed to melt rapidly in the flame. It does not really melt, but it merely dissolves in the minute drops of melted steel carried along by the gaseous current.

A Series of New Compounds—Chromosulphuric Acid and the Metallic Chromosulphates.—A. Recoura.—This paper will be inserted in full.

Researches on the Application of the Measurement of Rotatory Power to the Determination of the Compounds formed by the Aqueous Solutions of Perseite with Sodium and Ammonium Molybdates.—D. Gernez.—The rotation of the aqueous solution which is $-0^{\circ} 11'$, becomes positive on the addition of a quantity of salt which represents about 1-150th of the molecular weight of the molybdate. It increases by equal quantities if we add to the same volume equal quantities of salt, which leads us to admit that for each of these weights there takes place a combination with corresponding weights of perseite. The rotation which increases very regularly until we have added a quarter of the molecular weight of the molybdate, reaches a maximum value

for a quantity a little greater than $\frac{6.75}{24}$ of the molecular weight. These proportions would correspond to combination of 1 mol. of perseite and 1969 mols. of molybdic acid if we admit the formulæ—

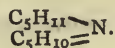


—representing respectively the composition of perseite and of acid sodium molybdate. But on examining closely the results of the experiment, it appears that for 2 mols. of molybdic acid the weight of salt corresponding

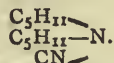
would be $\frac{6.857}{24}$ of the molecular weight; but for the addition of this quantity of salt the rotation observed, $7^{\circ} 5'$, is inferior to the rotation which corresponds to $\frac{6.75}{24}$.

We may, however, interpret these results, as the author has done in case of mannite and of sorbite, remarking that whilst molybdic acid alone has a very decided action upon perseite, acid sodium molybdate does not at all affect its rotatory power. We are thus led to infer that acid sodium molybdate acts by the excess of molybdic acid which it contains. Beyond the maximum the rotation gradually decreases, which indicates that there is a dissociation of the compound previously formed and a tendency towards new equilibria. The results of experiments made with perseite and acid ammonium molybdate lead to identical conclusions.

Action of Soda and Potassium Cyanide upon Chlorodiamylamine.—A. Berg.—The reaction of alcoholic soda upon chlorodiamylamine leads to the formation of amylamylidenamine—



The product of the reaction of potassium cyanide is diamylecyanamide—



If treated with hydrylic acid at 160° it is split up into carbonic acid, ammonia, and diamylamine.

On Metaphenyltoluene.—G. Perrier.—Of the three isomeric phenyltoluenes which theory foresees, the ortho has been studied by Barbier, and the para by Carnelley and Thomson. The author has obtained the meta-compound by causing an excess of sodium to react upon a mixture of equal mols. of metatoluenolene and of phenyl bromide dissolved in anhydrous ether, and heated for about 105 hours in a reflux apparatus to between 40° and 50°. The liquid is freed from ether and submitted to distillation. The product passing over between 245° and 275° is collected. It consists of diphenyl and the new hydrocarbon. It is submitted to the action of a mixture of ice and snow, when the chief part of the diphenyl crystallises. After a series of distillations followed by refrigerations with methyl chloride, a liquid is obtained, which, after distillation over sodium, did not combine with Fritzsche's reagent, and had the constant boiling-point 270°, and the composition $\text{C}_{14}\text{H}_{12}\text{O}_7$.

The Formation Heats of the Potassium Carballoylates.—G. Massol.—A thermo-chemical paper, not admitting of useful abstraction.

Specific Gravity of Textile Fibres.—M. de Chardonnet.—The author considers that Leo Vignon's method does not give the true density of the fibres, because the occluded air is not completely eliminated. The results given by Leo Vignon are too low; for cotton he gives the figure 1.50 instead of 1.95; for wool 1.30 instead of 1.61.

Detection of Resin Oil in Oil of Turpentine.—M. Zune.—If the latter oil is pure the difference between the index of the first quarter of the distillate and that of the last quarter should not exceed 400 units of the fifth decimal place, and will be almost always below 350. The presence of even one per cent will raise it to more than 600 units.

Comparative Nitrification of Humus and of Unaltered Organic Matter, and Influence of the Proportions of Humus upon Nitrification.—P. Pichard.—The use of marl is much preferable to that of lime on account of its property of retaining ammonia, of fixing the atmospheric nitrogen more abundantly.

Medical Utilisation of Alternating Currents of a High Potential.—G. Gautier and J. Larat.—The ozone produced by electric discharges is, in fact, largely mixed with nitrous products. The gas seems to a certain extent poisonous, as it readily occasions vertigo, angina, and even bronchitis.

The Composition of Hæmocyanine.—A. B. Griffiths.—Hæmocyanine may be precipitated from the blood of *Homarus*, *Cancer*, and *Sepia*, by magnesium sulphate. The precipitate is dissolved in water and re-precipitated by alcohol. Its composition is $\text{C}_{867}\text{H}_{1303}\text{N}_{223}\text{CuS}_4\text{O}_{258}$. Hæmocyanine has a very uniform composition, differing in this respect from hæmoglobine. It is also much more stable.

The Ptomaines in Some Infectious Diseases.—A. B. Griffiths.—The method pursued by the author for extracting the urinary ptomaines has been already described in the *Comptes Rendus*, vol. xciii., p. 656. 1. *Measles*.—The ptomaine extracted from the urine of the patients is

a white, crystalline substance, soluble in water, with an alkaline reaction. Its chloroplatinate forms microscopic crystalline needles. Mercuric chloride yields a double salt, almost insoluble in water, which crystallises in prismatic needles. This ptomaine is also precipitated by the picric, phosphomolybdic, and phosphotungstic acids. Its composition is expressed by the formula $\text{C}_3\text{H}_5\text{N}_3\text{O}$. It is very poisonous. 2. The ptomaine obtained from the urine in cases of whooping-cough is white, crystalline, and soluble in water. It forms a hydrochlorate and a chloraurate, it gives a white precipitate with phosphomolybdic acid, a yellow precipitate with picric acid, and a maroon precipitate with tannin. Its composition is $\text{C}_5\text{H}_{10}\text{NO}_2$. Afanassieff's bacillus found in matter expectorated in whooping-cough has the same composition. Neither of the two ptomaines described above is found in normal urine.

MISCELLANEOUS.

Crystal Palace Electrical Exhibition.—The following gentlemen have kindly consented to serve on the jury for this Exhibition:—Prof. W. Grylls Adams, D.Sc., F.R.S., Prof. W. E. Ayrton, F.R.S., Mr. Shelford Bidwell, M.A., F.R.S., Mr. Conrad Cooke, M.Inst.E.E., Prof. W. Crookes, F.R.S., Mr. W. B. Esson, M.Inst.E.E., Major-Gen. Festing, R.E., F.R.S., Prof. George Forbes, M.A., F.R.S., Capt. Sir Douglas Galton, K.C.B., D.C.L., F.R.S., Dr. J. H. Gladstone, F.R.S., Mr. J. H. Greathead, M.Inst.C.E., Mr. Charles Hall, M.Inst.E.E., Prof. D. E. Hughes, F.R.S., Sir Henry Mance, C.I.E., Mr. W. H. Massey, M.Inst.C.E., Mr. W. H. Preece, F.R.S., Mr. A. Reckenzaun, Prof. Henry Robinson, M.Inst.C.E., Capt. Sankey, R.E., M.Inst.E.E., Mr. C. E. P. Spagnoletti, M.Inst.C.E., Mr. James Swinburne, M.Inst.E.E., Prof. Silvanus Thompson, D.Sc., F.R.S., Mr. J. Tomlinson, M.Inst.C.E., Prof. W. C. Unwin, B.Sc., M.Inst.C.E., Major-General Webber, C.B., R.E., Mr. J. W. Wilson, M.Inst.C.E.

MEETINGS FOR THE WEEK.

- MONDAY, 21st.**—Medical, 8.30.
— Society of Arts, 8. "The Uses of Petroleum in Prime Movers," by Prof. William Robinson, M.E. (Cantor Lectures).
TUESDAY, 22nd.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
— Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8. Exhibition of Old Silver Prints, Mr. Dallmeyer will show his Telephotographic Lens. "On Copying Inclined Pictures," by Mr. Chapman Jones.
WEDNESDAY, 23rd.—Society of Arts, 8. "Manufacture and Industrial Application of Flexible Tubing," by Gilbert R. Redgrave.
— Geological, 8.
THURSDAY, 24th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Epidemic Waves," by B. Arthur Whitelegge, M.D., B.Sc.
— Society of Arts, 8. "The Opium Question," by G. H. M. Batten.
FRIDAY, 25th.—Royal Institution, 9. "Posy Rings," by John Evans. D.C.L., LL.D., &c.
— Physical, 5. "Electromotive Forces of Gold and Platinum Cells," by Prof. Herron. On a New Instrument for Showing the Effects of Persistence of Vision," by E. S. Bruce, M.A. "Some Electrical Instruments," by R. W. Paul.
SATURDAY, 26th.—Royal Institution, 3. "Dramatic Music, from Shakspeare to Dryden," by Prof. J. F. Bridge, Mus. Doc.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1687.

CHANGES OF ELECTROMOTIVE FORCE, VOLUME, AND TEMPERATURE BY MIXING ELECTROLYTES.*

By Dr. G. GORE, F.R.S.

In a paper on "Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c., of Electrolytes" (*Philosophical Magazine*, August, 1891, p. 157), I have shown the effects of dilution upon the temperature and total volume of the liquids, and upon the mean amount of electromotive force of a voltaic couple immersed in them. In the present case, I have examined in a similar manner the effects of mixing electrolytes upon the same phenomena, and in order to obtain some new information respecting the chemical substitution of acids and the double decomposition of salts, I have employed pairs of what I venture to term "isomeric mixtures. The mixtures I employed were all of them dissolved in distilled water, and are divided into two groups, viz., 1st Section, acids + salts, for examining the substitution of acids; and 2nd, salts + salts, for examining double decomposition.

All the substances employed were taken in the proportions of their chemical equivalents, and in each case the equivalent weight in grains of each ingredient was dissolved in 1800 grains of water; and, after measuring their separate amounts of electromotive force, the two solutions were mixed, and the changes in their temperature, total volume, and mean amount of electromotive force ascertained; the quantity of each salt usually employed in a thermal measurement varied from 30 to 100 grains. A cadmium-platinum voltaic couple and a thermo-electric pile of german silver and iron were used for measuring, by the method of opposition, the changes of electromotive force at ordinary atmospheric temperature, and the measurements are given in volts. The thermometer employed was capable of measuring 0.01° C. Details of the mode of experimenting and of measuring the changes attending the act of mixing has already been given in the paper referred to, and in another one on "A Method of Measuring Loss of Energy Due to Chemical Union, &c." (see *Phil. Mag.*, Jan., 1892, p. 28).

A series of tables of isomeric mixtures of acids + salts are given in the full paper, showing changes of mean electromotive force, total volume, and temperature of 15 isomeric couples of mixed liquids, attending the expulsion of one acid from a salt by means of another.

A circumstance to be noticed in these tables is, that every mixture suffered a change either of total volume, temperature, or mean amount of electromotive force, or of all three, during the mixing; thus showing that with each pair of ingredients either a chemical or a molecular change had occurred. And another fact to be observed is that in every instance each of the two mixtures of an isomeric couple gave the same amount of electromotive force. From the latter we may conclude that, in the entire fifteen cases, each of the two pairs of ingredients formed the same final product during the mixing; the two started with different amounts of energy, but both arrived at the same final condition.

The difference of behaviour, both as regards change of electromotive force, of total volume, and of temperature between the two mixtures of an isomeric couple is, in nearly every instance of the series, quite manifest; in

nearly all cases, the one mixture gives a greater gain of electromotive force than the other; and the one gives an increase and the other a decrease of temperature; and, in most cases the one gives a contraction and the other an expansion of volume; the one which gave the smallest gain of electromotive force usually also gave the greatest contraction of volume. Out of the thirty mixtures, twenty-nine gave a gain, and one gave a loss of electromotive force; this proportion would differ with each different positive metal used in the voltaic couple. (See "A Method of Measuring Loss of Energy Due to Chemical Union, &c., of Electrolytes," *Phil. Mag.*, Jan., 1892, p. 28).

All change is relative, if we view the numbers not as actual amounts of opposite kinds of action, but only as relative ones of the same kind, i.e., each loss of electromotive force as being only a smaller gain, each contraction of volume as only a smaller expansion, and each increase of temperature as only a smaller decrease; the three series of changes are found to agree with each other in thirty-three out of the forty-five possible ways of comparing them. Thus, the largest gain of mean electromotive force is attended by the greatest expansion of volume (and increased freedom of molecular motion) in nine cases, and by the largest decrease of temperature (and absorption of heat) in fourteen cases, and the largest expansion of volume is accompanied by the greatest decrease of temperature in ten cases. The connection between mean electromotive force, mean specific gravity, and latent heat is thus distinctly shown, and more clearly than in cases of simple dilution of acids and salts by water in a previous research (see "Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c., of Electrolytes," *Phil. Mag.*, Aug., 1891, p. 157). Some of the exceptional cases may probably be explained by assuming that one liquid of one mixture dilutes the other one, and thus allows greater freedom of molecular motion, which more than compensates larger contraction of volume or greater loss of heat.

With regard to the relative degrees of energy of chemical action in the two mixtures of each isomeric couple, the tables supply three different kinds of evidence, viz., change of volume, of temperature, and of mean electromotive force; and, in accordance with well-known general truths in chemistry, we may infer that the compound which during the act of mixing gives the largest proportion of contraction (or smallest expansion) of volume, the largest evolution (or smallest absorption) of heat, and the greatest loss (or smallest gain) of mean electromotive force is probably the one in which chemical union is the strongest. In each of the fifteen instances of isomeric couples, the mixture in which the strongest molecular and chemical union is supposed, according to this view, to occur is placed the first.

With regard also to the question of chemical substitution of one acid by another, and which of two acids is the strongest whilst in a state of solution, if the relative degree of strength of chemical action are truly though only approximately represented by the amounts of contraction of volume, of evolved heat, and decrease of mean electromotive force, we may infer that, in the examples given, sulphuric acid has a greater power of expelling nitric acid than nitric has of expelling sulphuric, that it has greater power of expelling hydrochloric acid than the reverse, and of expelling acetic acid than the reverse; that hydrochloric acid has greater power of expelling nitric acid than the opposite, and that hydrochloric acid has greater power of expelling hydrobromic acid than the reverse. With regard to the couple No. 4, however, according to J. Thomsen, "when soda, nitric acid, and sulphuric acid mutually react in equivalent quantities in a dilute solution, two-thirds of the soda combines with the nitric acid, and one-third with the sulphuric acid," and "nitric acid in aqueous solution is a stronger acid than sulphuric" ("Principles of Chemistry," by P. Muir, p. 437); according to Ostwald, also, the strongest acid is

* Abstract prepared by the Author of a Paper read before the Birmingham Philosophical Society, and recently published in vol. viii., Part I, p. 23 of the *Proceedings* of the Society.

the one which takes the largest proportion of base ("Outlines of General Chemistry," translated by J. Walker, p. 324). When this couple, in very dilute solutions, was examined by the voltaic balance method, the mixture $\text{H}_2\text{SO}_4 + 2\text{NaNO}_3$, during the mixing at once changed to the final state; whilst the other one, $2\text{HNO}_3 + \text{Na}_2\text{SO}_4$, required the assistance of heat, as if the action of the sulphuric acid was stronger than that of the nitric (see *Phil. Mag.*, Oct., 1889, p. 290). The most fundamental question, however, is probably not what are the relative strengths of different acids, but what are the relative directions and velocities of the molecular motions of the substances?

In the next section (B), mixtures of salts with salts were similarly examined. In this case, the magnitudes of nearly all the changes were much smaller than in Section A, salts + acids. Each of the twenty mixtures, however, showed an alteration either of mean electromotive force, total volume, or temperature due to the act of mixing; thus indicating the occurrence of either a molecular or a chemical change in every instance.

In each of the ten isomeric couples examined, the amount of electromotive force produced by each of the two mixtures was the same, thus indicating that they had both passed to the same final state and attained the same molecular or chemical composition.

The much larger proportion of cases of loss to those of gain of mean electromotive force in this section than in Section A was no doubt due to the employment of salts + salts instead of acids + salts. A similar result was obtained in a previous research, in which isomeric mixtures were not used (see "A Method of Measuring Loss of Energy during the Chemical Union, &c., of Electrolytes," *Phil. Mag.*, Jan., 1892, p. 28).

The three series of changes of volume, temperature, and electromotive force in this section largely agree with each other, but the agreement is generally less distinct than with the series of mixtures of acids + salts.

General Remarks.

The results obtained in this research, and in the one on "A Method of Measuring Loss of Energy during Chemical Union, &c., of Electrolytes" (*Phil. Mag.*, Jan., 1892), show that when one electrolyte is added to another each electrolyte so affects the other during the act of mixing that the total volume, the mean amounts of latent heat and of electromotive force (and probably of other properties of the liquids, such as refractive power, transparency to various kinds of radiant energy, &c.) of each of the two substances are altered. Similar changes of volume and of temperature are already known.

The fact that the three classes of results obtained in this research extensively agree with each other indicates that they are connected with some very fundamental property of matter; whilst the absence of apparent agreement between them in a minority of cases is probably due to some minor circumstance. The lack of perfect agreement between the three different classes of effects, both with acids + salts and with salts + salts, shows that the phenomena are less simple than at first sight they appear to be. As the molecules of all substances are in a ceaseless state of motion, it is probable that the alterations of volume, temperature, and electromotive force are results of changes of amount of opposite motions of the molecules of the two mixed substances. According to this view, the loss of heat and the production of chemical and voltaic action are due to neutralisation and other changes of molecular motion.

If the changes of volume, temperature, electromotive force, and total molecular energy are results of neutralisation of opposite or incompatible motions of the two substances, we may infer that in a case of chemical union the molecular motion of the constituent A of a mixture of electrolytes so alters that of the one B, and the latter so affects that of the former during the act of mixing, a

usually to decrease the total volume, the latent heat, the mean amount of that portion of the molecular motion of each dissolved electronegative substance which is incompatible with the molecular motion of the positive metal; and consequently, also, the mean amount of electromotive force. The results obtained by experiment in this research, and in the one referred to (*ibid.*), show that if A is an acid and B is a base, the total volume, the latent heat, and the mean amount of electromotive force are usually largely decreased. If A and B are both salts, these effects are usually feeble and variable. If A is an acid and B is a salt, those effects are usually increased in one mixture of an isomeric couple and decreased in the other. And if A is a halogen and B is a salt, the increase in one mixture of such a couple is frequently greater, but if heat is then applied a large decrease usually occurs (*ibid.*).

These effects may be largely explained by the opposite influences of chemical union and dilution upon the degree of freedom of molecular motion, and, consequently, upon the electromotive force; chemical union usually decreases and dilution usually increases the mean amount of electromotive force; but the former produces a greater and more profound change than the latter. In nineteen cases out of twenty, the dilution of an acid or a salt solution by water was attended by an increase of mean amount of electromotive force (see "Relations of Volta Electromotive Force to Latent Heat, Specific Gravity, &c., of Electrolytes," *Phil. Mag.*, Aug., 1891, p. 157; also "A Relation of Electromotive Force to Equivalent Volume and Molecular Distance of Substances," *Proc. Birm. Phil. Soc.*, 1892, vol. viii., Part 1), as if the substances were in some degree "dissociated," or had acquired a greater degree of freedom of molecular motion; the latter appears the most likely. Similarly, when the ingredients of two different solutions which were mixed did not chemically unite, but their solutions merely diluted each other, the increase of mean electromotive force was greater (or the loss of it was less) in proportion as the degree of intimacy of union was less, and the uncombined or feebly combined electronegative substance had greater molecular and chemical energy; thus, in the case of addition of an acid to a salt, there was often a gain of mean electromotive force, because there was practically a dilution and an increased freedom of molecular motion of the acid unattended by chemical union; and if a halogen, instead of an acid, was used the gain was still greater, provided no chemical union occurred (see "A Method of Measuring Loss of Energy by Chemical Union, &c., of Electrolytes," *Phil. Mag.*, Jan., 1892). If, however, an acid solution was added to one of a base, there was usually a large loss of mean electromotive force, because there was chemical union, contraction of volume, loss of heat, and diminished freedom of molecular motion (*ibid.*).

The fundamental conditions of the phenomena are relative velocity and direction of molecular motion. The greater the velocity of the molecules of the electronegative constituent of the liquid, the greater usually is the electromotive force; thus, the halogens have greater molecular velocity, and produce a greater effect than acids, and acids than salts, and act more strongly upon the electropositive metal. The more opposite also in direction or incompatible the molecular motion of the electronegative constituent of the liquid, after mixing, is to that of the positive metal, the greater usually is the electromotive force; and the more opposite the molecular motions of an acid are to those of a base, the larger usually is the loss of energy and loss of mean amount of electromotive force during the union of those substances.

Relative degree of freedom of molecular motion, by influencing the molecular velocity has great effect, thus:—
1. Diluting an acid or saline solution with water usually produces an increase of mean amount of electromotive force, especially with strong acids; actual trial gave nineteen out of twenty cases (see "Relation of Volta Electromotive

Force to Latent Heat, Specific Gravity, &c., of Electrolytes," *Phil. Mag.*, Aug., 1891, p. 157); 2. Add a solution of a salt to one of a salt, and there is but little gain of mean electromotive force, because the electronegative constituents of the salts, being chemically united to their respective bases, have but little freedom of molecular motion, and the effect of dilution of one liquid by the other is therefore small; 3. Add a solution of an acid to one of a salt, and both the mean electromotive force and the gain of mean amount of that force are larger, because free acid possessing greater velocity of molecular motion is present and dilution of one liquid by the other increases that motion; 4. Add a dissolved halogen to a dissolved salt, and there is usually a still greater gain of electromotive force and of mean amount of that force, because a free halogen has usually greater velocity of molecular motion than a free acid. If, however, we heat this latter mixture, chemical union usually occurs, freedom of molecular motion is diminished, and there is a large decrease both of electromotive force and of mean amount of that force; 5. Add a solution of an acid to one of a base and there is a great loss of heat, attended by large decrease of velocity and freedom of molecular motion and of mean amount of electromotive force, which more than neutralises the increased freedom of motion caused by the dilution.

If we examine the influence of the action of an acid upon a base with regard to its subsequent action upon the positive metal, we find that the larger the amount of molecular motion of the acid incompatible with that of the base, and the larger the loss of such motion as heat during mixture, the smaller usually is the amount of residuary molecular motion incompatible with that of the positive metal, the greater usually is the loss of mean amount of electromotive force, and the smaller is the actual electromotive force.

According to the foregoing explanation, in cases of gain of mean electromotive force, the changes of molecular motion during mixing a pair of electrolytes are such that the proportion of energy of the electronegative constituent of the mixture which is opposed to, and incompatible with, that of the positive metal of the voltaic couple becomes larger, and in cases of loss, the reverse. It does not, however, necessarily follow from this that the total amount of molecular motion of the liquid, or of the electronegative substances dissolved in it, is always greater when the mean electromotive force is increased, because we know by experiment that in some exceptional cases the latter is greater after the two liquids have lost molecular motion in the form of heat than previously (*ibid.*). Some of the exceptional cases may probably be explained by the increase of mean electromotive force attending dilution.

Upon the basis of Newton's third law of motion, that action and reaction are always equal, we may in all cases conclude that the loss of energy in the form of heat during chemical union, and the absorption of heat during the mixture of any two electrolytic substances, is equally divided between them.

As the degree of volta electromotive force is a direct result of, and inseparably connected with, strength of chemical action of the electronegative constituent of the liquid upon the positive metal, the foregoing general remarks on the relations of molecular motion to electromotive force apply largely to the relations of such motion to chemical action of that constituent on that metal, and the measurements of electromotive force are, to a certain extent, therefore, also measurements of strength of chemical action.

The chief new truth disclosed by this research is the distinct connection between changes of total volume, total heat, molecular motion, and mean amount of electromotive force. All the results obtained in this research help to confirm the existence of a mechanical basis of voltaic and chemical action.

THE CHROMOSULPHATES.

By C. F. CROSS.

A RECENT notice of the investigations of A. Recoura (*Comptes Rendus*, cxiv., 477) upon the above salts, which are described as "a series of new compounds" (*CHEM. NEWS*, lxx., 137) has attracted my attention. The author appears to have overlooked some researches published ten years ago bearing on this subject ("The Reaction of Chromic Anhydride with Sulphuric Acid," by Cross and Higgin, *Chem. Soc. Journ.*, xli., 113), establishing as they do the existence of chromosulphates of very considerable stability. The compounds which we described were prepared by heating CrO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ with H_2SO_4 at a temperature approaching the boiling-point of the latter. There appears to be a complete reduction of the CrO_3 to Cr_2O_3 under these conditions, the sesquioxide reacting with the sulphuric acid to form acid sulphates, which separate as amorphous precipitates in the acid liquid. From the CrO_3 we obtained chromosulphate of a lavender colour, somewhat variable in composition, but approximating to the formula $4\text{Cr}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 7\text{H}_2\text{SO}_4$; from the potassium salt, green compounds, generally similar in composition to the above, but with a proportion of the Cr_2O_3 substituted by K_2O . The analyses of these compounds gave the following mean numbers:—

	From CrO_3 .	From $\text{K}_2\text{Cr}_2\text{O}_7$.
Cr_2O_3	34.8	26.6
SO_3	58.2	59.3
H_2O	7.2	7.1
K_2O	—	6.9
	100.2	99.9

In both, the ratio of acid to base is greater than the normal, and from the conditions of their formation we must regard the H_2O as present in the form of H_2SO_4 . The compounds obtained from CrO_3 lose nearly the whole of their SO_3 on ignition, but both groups of sulphates are very resistant to the action of alkalis. It is evident that these results may be taken with those of M. Recoura as showing that some exceptional relationship obtains between CrO_3 and H_2SO_4 through a very wide range of conditions.

The later investigations of M. Recoura appear to have satisfactorily elucidated this relationship under the condition of the solution of the reacting molecules in water, and at the same time they reopen the problem which we attacked from a purely empirical standpoint, viz., the conditions of molecular equilibrium obtaining between Cr_2O_3 and H_2SO_4 in presence of excess of the latter and at the temperature of its boiling point. M. Recoura's observations supply a working hypothesis, with which I shall be enabled to reinvestigate the anhydrosulphates above described with some promise of solving the problem in question.

4, New Court, London, E.C.
March 19, 1892.

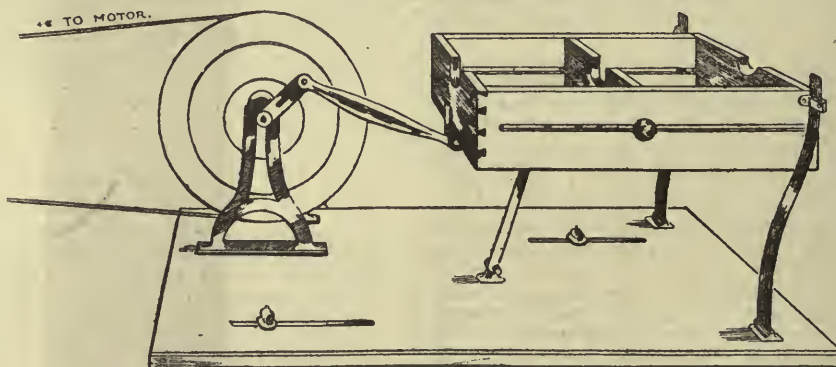
Royal Institution.—The following are the Lecture Arrangements after Easter:—Prof. T. G. Bonney, two lectures on "The Sculpturing of Britain—its Later Stages" (the Tyndall Lectures); Mr. Frederick E. Ives, two lectures on "Photography in the Colours of Nature"; Prof. R. C. Jebb, M.P., three lectures on "Some Aspects of Greek Poetry"; Prof. Dewar, four lectures on "The Chemistry of Gases"; Mr. R. G. Moulton, three lectures on "Faust"; Mr. E. Dannreuther, four lectures on J. S. Bach's "Chamber Music" (with many musical illustrations); Prof. H. Marshall Ward, three lectures on "Some Modern Discoveries in Agricultural and Forest Botany" (illustrated by lantern). The Friday Evening Meetings will be resumed on April 29th, when a discourse will be given by Dr. William Huggins on "The New Star in Auriga"; succeeding discourses will probably be given by Captain Abney, Dr. B. W. Richardson, Mr. J. Wilson Swan, Sir James Crichton-Browne, Mr. Ludwig Mond, Prof. Dewar, and other gentlemen.

ON A SIMPLE LABORATORY SHAKER.*

By WYNDHAM R. DUNSTAN and T. S. DYMOND.

IN most laboratories, especially where research in organic chemistry is being carried on, the need for some mechanical arrangement for shaking is constantly felt. The extraction of solids with various liquids, the desiccation of organic liquids with a solid drying agent, the chemical action of a liquid on a substance not freely soluble in it, are a few out of many instances where time and trouble may be saved and greater efficiency secured by the employment of a mechanical contrivance for shaking. In the Research Laboratory of the Pharmaceutical Society such a machine, which works almost noiselessly, is now in constant use.

Having found that the arrangements for the purpose which are usually sold by apparatus-makers were unsuited to all our requirements, we devised a simple shaking machine, which in a form perfected by more than a year's experience, we now wish to bring under the notice of the Society. A very few words of explanation are necessary,



since the principle and mode of working of the shaker are readily apparent from the drawing.

It consists of a wooden truck into which can be firmly fixed, by means of a sliding partition, a bottle or other vessel of any size up to that of a Winchester quart. This truck is supported underneath, near the front, by a rod which is capable of moving backwards and forwards on a pivot. At the back, the truck is supported by two flexible steel laths, one end of each being clamped to either side of the truck, the other end being firmly fitted in the base-board of the machine. The necessary to and fro motion is communicated to the truck in the usual manner by means of a crank connected with a revolving wheel and joined to the truck by an iron or wooden rod. This rod can be attached to the crank at different distances from the axle, so that the extent of the excursions made by the truck may be varied. A cord from a water or other small motor passes over the wheel, which is grooved at three distances from the centre so that the rate of motion may be regulated. In order to avoid the necessity of altering the length of the cord which passes from the motor to the wheel, the base-board of the apparatus is provided with slots and thumbscrews by means of which it may be securely fixed to the bench at the required distance from the motor.

The shaker may be obtained from Messrs. Baird and Tatlock, Cross St., Hatton Garden, E.C.

Novel Synthesis of Tartaric Acid.—P. Genviesse.

—By treating glyoxylic acid with nascent acid the author has obtained racemic acid. He thinks it not impossible that in nature tartaric acid is formed in an analogous manner.—*Comptes Rendus*, cxiv., No. 10.

THE FARADAY CENTENARY.

THE Faraday Centenary, in honour of Michael Faraday (born September 22, 1791), was celebrated at the Royal Institution of Great Britain on Wednesday, June 17, 1891, the Prince of Wales, K.G., F.R.S., in the chair.

The PRINCE OF WALES opened the proceedings with the following Address:—

Ladies and Gentlemen,—I can well remember that two-and-twenty years ago I had the high privilege of presiding at a meeting here. That meeting was a very large one, and included many of the most eminent scientific men of the day. Among those present on that occasion, I remember, were the illustrious chemists, Prof. Dumas, Sir Edward Sabine, Sir Roderick Murchison, Sir Henry Holland,—a very old personal friend of mine,—Dr. Bence Jones, Mr. Warren de la Rue and many others, who I regret to say have now passed away. The object of our meeting on that occasion was to select a suitable memorial to the memory of the great Faraday, the eminent chemist and philoso-

pher, who, I may say, was also the founder of modern electricity. As you are well aware, the fine statue by Foley, which is in the hall below, was, we thought, a suitable memorial to that great man. As for myself personally, I feel proud to think that in the days of my boyhood my brother and myself used to attend his chemical lectures here about Christmas time, and I shall ever remember the admirable and lucid way in which he delivered those lectures to us who were mere boys, and gave us a deep interest in chemistry which we kept up for many years, and which I had the opportunity of practising at the University of Oxford. I can only regret that I have not since had the time to pursue that interesting science. To-day is a memorable day, for this year we celebrate the centenary of the birth of that great man; and we all of us have reason to feel grateful that two such eminent men as Lord Rayleigh and Prof. Dewar should have consented to give lectures on the work of the great Faraday. I have only now to beg Lord Rayleigh to give us his address.

LORD RAYLEIGH said that the man whose name and work they were celebrating was identified in a remarkable degree with the history of this Institution. If they could not take credit for his birth, in other respects they could hardly claim too much. During a connection of fifty-four years, Faraday found there his opportunity, and for a large part of the time his home. The simple story of his life must be known to most who heard him. Fired by contact with the genius of Davy, he volunteered his services in the laboratory of the Institution. Davy, struck with the enthusiasm of the youth, gave him the desired opportunity, and, as had been said, secured in Faraday not the least of his discoveries. The early promise was, indeed, amply fulfilled, and for a long period of years by his discoveries in chemistry and electricity Faraday

* Exhibited at a meeting of the Chemical Society, March 6, 1892.

maintained the renown of the Royal Institution and the honour of England in the eye of the civilised world. He should not attempt in the time at his disposal to trace in any detail the steps of that wonderful career. The task had already been performed by able hands. In their own *Proceedings* they had a vivid sketch from the pen of one whose absence that day was a matter of lively regret. Dr. Tyndall was a personal friend, had seen Faraday at work, had enjoyed opportunities of watching the action of his mind in face of a new idea. All that he could aim at was to recall in a fragmentary manner some of Faraday's great achievements, and, if possible, to estimate the position they held in contemporary science.

Whether they had regard to fundamental scientific import, or to practical results, the first place must undoubtedly be assigned to the great discovery of the induction of electrical currents. He proposed first to show the experiment in something like its original form, and then to pass on to some variations, with illustrations from the behaviour of a model, whose mechanical properties were analogous. He was afraid that these elementary experiments would tax the patience of many who heard him, but it was one of the difficulties of his task that Faraday's discoveries were so fundamental as to have become familiar to all serious students of physics.

The first experiment required them to establish in one coil of copper wire an electric current by completing the communication with a suitable battery; that was called the primary circuit, and Faraday's discovery was this:—That at the moment of the starting or stopping of the primary current in a neighbouring circuit, in the ordinary sense of the words completely detached, there was a tendency to induce a current. He had said that those two circuits were perfectly distinct, and they were distinct in the sense that there was no conducting communication between them, but, of course, the importance of the experiment resided in this—that it proved that in some sense the circuits were not distinct; that an electric current circulating in one does produce an effect in the other,—an effect which is propagated across a perfectly blank space occupied by air, and which might equally well have been occupied by vacuum. It might appear that that was a very simple and easy experiment, and of course it was so in a modern laboratory, but it was otherwise at the time when Faraday first made it. With all his skill, Faraday did not light upon the truth without delay and difficulty. One of Faraday's biographers thus wrote:—"In December 1824, he had attempted to obtain an electric current by means of a magnet, and on three occasions he had made elaborate and unsuccessful attempts to produce a current in one wire by means of a current in another wire, or by a magnet. He still persevered, and on August 29, 1831,—that is to say, nearly seven years after his first attempts,—he obtained the first evidence that an electric current induced another in a different circuit." On September 23rd, he writes to a friend, R. Phillips:—"I am busy just now again with electro-magnetism, and think I have got hold of a good thing, but cannot say; it may be a weed instead of a fish that, after all my labour, I at last haul up." We now know that it was a very big fish indeed. Lord Rayleigh proceeded to say that he now proposed to illustrate the mechanics of the question of the induced current by means of a model (see figure), the first idea of which was due to Maxwell. The one actually employed was a combination known as Huygen's gear, invented by him in connection with the winding of clocks. Two similar pulleys, A B, turn upon a piece of round steel fixed horizontally. Over these is hung an endless cord, and the two bights carry similar pendant pulleys, C D, from which again hang weights, E F. The weight of the cord being negligible, the system is devoid of potential energy; that is, it will balance, whatever may be the vertical distance between C and D. Since either pulley, A B, may turn independently of the other, the system is capable of two independent motions. If A B turn in the same direction

and with the same velocity, one of the pendant pulleys, C D, rises, and the other falls. If, on the other hand, the motions of A B are equal and opposite, the axes of the pendant pulleys and the attached weights remain at rest. In the electrical analogue the rotatory velocity of A corresponds to a current in a primary circuit, that of B to a current in a secondary. If, when all is at rest, the rotation of A be suddenly started, by force applied at the handle or otherwise, the inertia of the masses E F opposes their sudden movement, and the consequence is that the pulley B turns *backwards*, i.e., in the opposite direction to the rotation imposed upon A. This is the current induced in a secondary circuit when an electromotive force begins to act in the primary. In like manner, if A, having been for some time in uniform movement, suddenly stops, B enters into motion in the direction of the former movement of A. This is the secondary current on the break of the current in the primary circuit. It might perhaps be supposed by some that the model was a kind of trick. Nothing could be further from the truth. The analogy of the two things



was absolutely essential. So far was this the case that precisely the same argument and precisely the same mathematical equations proved that the model and the electric currents behaved in the way in which they had seen them behave in the experiment. That might be considered to be a considerable triumph of the modern dynamical method of including under the same head phenomena the details of which might be so different as in this case. If they had a current which alternately stopped and started, and so on, for any length of time, they, as it were, produced in a permanent manner some of the phenomena of electrical induction; and if it were done with sufficient rapidity it would be evident that something would be going on in the primary and in the secondary circuit. The particular apparatus by which he proposed to illustrate those effects of the alternating current was devised by a skilful American electrician, Prof. Elihu Thomson, and he had no doubt it would be new to many. The alternating current was led into the electro-magnet by a suitable lead; if another electric circuit, to be called the secondary circuit, was held in the neighbourhood of that, currents would be induced and might be made manifest by suitable means. Such a secondary circuit he held in his hand and it was

connected with a small electric glow-lamp. If a current of sufficient intensity were induced in that secondary circuit it would pass through the lamp, which would be rendered incandescent. [Illustrating.] It was perfectly clear that there was no conjuring there; the incandescent lamp brightened up. One of the first questions which presented itself was, what would be the effect of putting something between? Experimenting with a glass plate he showed there was no effect, but when they tried a copper plate the lamp went completely out, showing that the copper plate was an absolute screen to the effect, whatever it might be. Experiments of that kind, of course in a much less developed and striking form, were made by Faraday himself, and must be reckoned amongst some of his greatest discoveries.

Before going further, he might remark on what strong evidence they got in that way of the fact that the propagation of the electric energy which, having its source in the dynamo downstairs, eventually illuminated that little lamp, was not merely along the wires, but was capable of bridging over and passing across a space free from all conducting material, and which might be air, glass, or equally well, vacuum. Another kindred effect of a striking nature, devised by Prof. Elihu Thomson, consisted in the repulsive action which occurred between the primary current circulating around a magnet and the current induced in a single hoop of aluminium wire. Illustrating this by experiment, he showed that the repulsion was so strong as to throw the wire up a considerable height. Those effects were commonly described as dependent upon the mutual induction between two distinct circuits, one being that primarily excited by a battery or other source of electricity, while the other occurred in a detached circuit. Many surprising effects, however, depended on the reactions which took place at different parts of the same circuit. One of these he illustrated by the decomposition of water under the influence of self-induction.

About the time the experiments of which he had been speaking were made, Faraday evidently felt uneasiness as to the soundness of the views about electricity held by his contemporaries, and to some extent shared by himself, and he made elaborate experiments to remove all doubt from his mind. He re-proved the complete identity of the electricity of lightning and of the electricity of the voltaic cell. He evidently was in terror of being misled by words which might convey a meaning beyond what facts justified. Much use was made of the term "poles" of the galvanic battery. Faraday was afraid of the meaning which might be attached to the word "pole," and he introduced a term since generally substituted, "electrode," which meant nothing more than the way or path by which the electricity was led in. "Electric fluid" was a term which Faraday considered dangerous, as meaning more than they really knew about the nature of electricity, and as was remarked by Maxwell, Faraday succeeded in banishing the term "electric fluid" to the region of newspaper paragraphs.

Diamagnetism was a subject upon which Faraday worked, but it would take him too long to go into that subject, though he must say a word or two. Faraday found that whereas a ball of iron or nickel or cobalt when placed near a magnet or combination of magnets would be attracted to the place where the magnetic force was the greatest, the contrary occurred if for the iron was substituted a corresponding mass of bismuth or of many other substances. The experiments in diamagnetism were of a microscopic character, but he would like to illustrate one position of Faraday's, developed years afterwards by Sir Wm. Thomson, and illustrated by him in many beautiful experiments, only one of which he now proposed to bring before them. Supposing they had two magnetic poles, a north pole and a south pole, with an iron ball between them, free to move along a line perpendicular to that joining the poles, then, according to the rule he had stated, the iron ball would seek an intermediate position, the place at which the magnetic force

was the greatest. Consequently, if the iron ball be given such a position, they would find it tended with considerable force to a central position of equilibrium; but if, instead of using opposite poles, they used two north poles, they would find that the iron ball did not tend to the central position, because that was not the place in which the magnetic force was the greatest. At that place there was no magnetic force, for the one pole completely neutralised the action of the other. The greatest force would be a little way out, and that, according to Faraday's observations, systematised and expressed in the form of mathematical law by Sir Wm. Thomson, was where the ball would go. (This was illustrated by experiment).

The next discovery of Faraday to which he proposed to call attention was one of immense significance from a scientific point of view, the consequences of which were not even yet fully understood or developed. He referred to the magnetisation of a ray of light, or what was called in more usual parlance the rotation of the plane of polarisation under the action of magnetic force. It would be hopeless to attempt to explain all the preliminaries of the experiment to those who had not given some attention to those subjects before, and he could only attempt it in general terms. It would be known to most of them that the vibrations which constituted light were executed in a direction perpendicular to that of the ray of light. By experiment he showed that the polarisation which was suitable to pass the first obstacle was not suitable to pass the second, but if by means of any mechanism they were able after the light had passed the first obstacle to turn round the vibration, they would then give it an opportunity of passing the second obstacle. That was what was involved in Faraday's discovery. (Experiment). As he had said, the full significance of the experiment was not yet realised. A large step towards realising it, however, was contained in the observation of Sir Wm. Thomson, that the rotation of the plane of polarisation proved that something in the nature of rotation must be going on within the medium when subjected to the magnetising force, but the precise nature of the rotation was a matter for further speculation, and perhaps might not be known for some time to come.

When first considering what to bring before them he thought, perhaps, he might include some of Faraday's acoustical experiments, which were of great interest, though they did not attract so much attention as his fundamental electrical discoveries. He would only allude to one point which, as far as he knew, had never been noticed, but which Faraday recorded in his acoustical papers. "If during a strong steady wind a smooth flat sandy shore with enough water on it, either from the receding tide or from the shingle above, to cover it thoroughly, but not to form waves, be observed in a place where the wind is not broken by pits or stones, stationary undulations will be seen over the whole of the wet surface. . . . These are not waves of the ordinary kind, they are (and this is the remarkable point) accurately parallel to the course of the wind." When he first read that statement many years ago he was a little doubtful as to whether to accept the apparent meaning of Faraday's words. He knew of no suggestion of an explanation of the possibility of waves of that kind being generated under the action of the wind, and it was, therefore, with some curiosity that two or three years ago at a French watering-place he went out at low tide on a suitable day when there was a good breeze blowing to see if he could observe anything of the waves described by Faraday. For some time he failed absolutely to observe the phenomenon, but after a while he was perfectly well able to recognise it. He mentioned that as an example of Faraday's extraordinary powers of observation, and even now he doubted whether anybody but himself and Faraday had ever seen that phenomenon.

Many matters of minor theoretic interest were dealt with by Faraday, and reprinted by him in his collected works. He was reminded of one the other day by a lamentable

accident which occurred owing to the breaking of a paraffin lamp. Faraday called attention to the fact, though he did not suppose he was the first to notice it, that by a preliminary preparation of the lungs by a number of deep inspirations and expirations, it was possible so to aerate the blood as to allow of holding the breath for a much longer period than without such a preparation would be possible. He remembered some years ago trying the experiment, and running up from the drawing-room to the nursery of a large house without drawing any breath. That was obviously of immense importance, as Faraday pointed out, in the case of danger from suffocation by fire, and he thought that possibly the accident to which he alluded might have been spared had the knowledge of the fact to which Faraday drew attention been more generally diffused.

The question has often been discussed as to what would have been the effect upon Faraday's career of discovery had he been subjected in early life to mathematical training. The first thing that occurred to him about that, after reading Faraday's works, was that one would not wish him to be anything different from what he was. I the question must be discussed, he supposed they would have to admit that he would have been saved much wasted labour, and would have been better *en rapport* with his scientific contemporaries if he had had elementary mathematical instruction. But mathematical training and mathematical capacity were two different things, and it did not at all follow that Faraday had not a mathematical mind. Indeed, some of the highest authorities had held (and there could be no higher authority on the subject than Maxwell) that his mind was essentially mathematical in its qualities, although they must admit it was not developed in a mathematical direction. With these words of Maxwell he would conclude:—"The way in which Faraday made use of his idea of lines of force in co-ordinating the phenomena of electric induction shows him to have been a mathematician of high order, and one from whom the mathematicians of the future may derive valuable and fertile methods."

Sir WILLIAM THOMSON, in moving a vote of thanks to Lord Rayleigh for his lecture, said that the Royal Institution was during the last part of Faraday's life, and during the whole of his scientific career, his home. The splendid results of Faraday's labours contributed in no small degree to the scientific glory of the Nineteenth Century, and helped to make it one of the most prolific periods in the world's history. Faraday was throughout animated solely by the love of knowledge. He freely gave his discoveries to mankind, and left it to others to turn them to practical and profitable account.

Sir GEORGE STOKES, in seconding the motion, said that he had had the honour of a personal acquaintance with Faraday, whose single-minded devotion to knowledge for its own sake was beyond all praise.

The vote of thanks was cordially passed.

Lord RAYLEIGH, in acknowledgment, said that it had been a great honour and a great responsibility which had been placed upon him. He remembered with gratitude the instruction which he had derived at Cambridge from Sir Gabriel Stokes, and felt deeply indebted to Sir William Thomson for all that he had learned from his writings and his conversation.

Sir FREDERICK BRAMWELL read the following letter from Dr. Tyndall:—

Hind Head House, Haslemere,
June 16, 1891.

DEAR SIR FREDERICK BRAMWELL,

As Faraday recedes from me in time, he becomes to me more and more beautiful. Anything, therefore, calculated to do honour to his memory must command my entire sympathy.

But the utmost liberty I can now allow myself is to be shifted from my bed to a couch and wheeled to a position near the window, from which I can see the bloom of the gorse and the brown of the heather.

Thus, considerations affecting the body only present an insuperable barrier to my going to London on Wednesday.

Yours very truly,
JOHN TYNDALL.

The DUKE OF NORTHUMBERLAND then asked the meeting to express its sense of the kindness of his Royal Highness in presiding, and said he had permission to read two letters written many years ago, proving how keen was the interest taken by him in the lessons he had received from Faraday. The letters were as follows, the first being addressed to Mr. Faraday, and the second to Mrs. Faraday on the occasion of her husband's death:—

Windsor Castle, January 16, 1856.

DEAR SIR,

I am anxious to thank you for the advantage I have derived from attending your most interesting lectures. Their subject I now feel is of great importance. I hope to follow the advice you gave us of pursuing it beyond the lecture room, and I can assure you that I shall always cherish with great pleasure the recollection of having been assisted in my early studies in chemistry by so distinguished a man.

Believe me, dear sir, yours truly,
ALBERT EDWARD.

Wiesbaden, September 10, 1867.

DEAR MRS. FARADAY,

Although I have not the pleasure of knowing you, I cannot resist sending you a few lines to tell you how deeply grieved and distressed I am to hear of the death of your husband, Professor Faraday. Having had the great pleasure of knowing him for some years, and having heard his interesting lectures already when quite a boy, I can fully appreciate how great the loss must be, not only to you, but to the whole country at large, where his name was deeply venerated by all classes. His name will not only be remembered as a great and distinguished scientific man, but also as a good man, whose excellent and amiable qualities were so universally known. Pardon me trespassing so soon on your great grief, and

Believe me, dear Mrs. Faraday, yours very sincerely,
ALBERT EDWARD.

The DUKE OF NORTHUMBERLAND continued: He thought they would all agree that that was a touching letter of condolence. His Royal Highness had now long been a patron of the Institution, and had watched its progress with interest, which he hoped would be continued. He trusted his Royal Highness would have the gratification of seeing the country prosper long under the rule of his august family, and of seeing the benefits of science resulting in the increased happiness of the people.

Sir W. GROVE seconded the resolution, and said he was possibly the only one in the room who had known Faraday in his prime. He wished they had been celebrating the centenary with Faraday alive.

The thanks of the meeting to His Royal Highness having been expressed by acclamation,

The PRINCE OF WALES acknowledged it as follows:—Ladies and Gentlemen, I feel that I cannot, out of courtesy to yourselves, and of the noble duke who has so kindly proposed the usual thanks, and to Sir William Grove who has given us an interesting speech, pass it by without expressing to you my warmest thanks. It is a great honour and privilege to me to preside on this most interesting and memorable occasion. I have now known this room for thirty-six years, and I agree with Sir William Grove in wishing that we were celebrating the centenary of Faraday alive, and not dead—that he was alive to spend his hundredth birthday among us. I feel every time I come into this room as if I can see him standing there at that table, where he gave his interesting lectures and experiments when I was a boy. I again tender my thanks

to you, as I do to Lord Rayleigh, for the most interesting lecture he has given.

There was an exhibition in the Library of memorials of Faraday kindly lent to the Institution by Miss Jane Barnard and others.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 3rd, 1892.

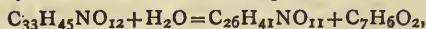
Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

Concluded from p. 140).

*116. "Contributions to our Knowledge of the Aconite Alkaloids. Part III. The Formation and Properties of Aconine and its Conversion into Aconitine. By Professor W. R. DUNSTAN and Dr. F. W. PASSMORE.

Owing to the uncertainty which exists with reference to the product of the hydrolysis of aconitine, the authors have re-investigated the subject, using a pure alkaloid. Wright and Luff have stated that when aconitine is hydrolysed the sole products are aconine and benzoic acid. More recently, however, Dragendorff and Jürgens have asserted that the hydrolysis occurs in two stages, their contention being that benzoic acid and an alkaloid identical with the picraconitine isolated by Wright and Luff from the roots of supposed *Aconitum napellus* are formed in the first stage, while in the second stage the picraconitine is hydrolysed into benzoic acid, methyl alcohol, and aconine, which last is the final product of hydrolysis.

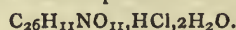
The authors have carefully hydrolysed pure aconitine by heating it with water in closed tubes at 150°, but have been unable to obtain at any stage either picraconitine or methyl alcohol. The alkaloid extracted from the solution by ether was proved to be a mixture of aconine with unaltered aconitine. Using pure aconitine, action occurs precisely in accordance with the equation—



leaving little doubt that aconitine is benzoyl-aconine.

Although attempts to establish the correctness of this inference by heating aconine with benzoic anhydride were without result, anhydroaconitine was eventually obtained by the interaction of aconine and ethylic benzoate at 130°: as the anhydro-compound is convertible into aconitine, the partial synthesis of the alkaloid thus effected leaves no doubt that it is benzoylaconine.

Up to the present time, neither aconine nor its salts have been obtained in a crystalline state. The authors have hitherto been unsuccessful in all their attempts to crystallise aconine, but they have succeeded in crystallising several of its salts, viz., the chlorhydride, bromhydride, sulphate, and nitrate. All these salts are very soluble in water, the chlorhydride being least soluble and the easiest to crystallise: it is best prepared by crystallisation from a mixture of alcohol and ether; when dried at 100° it melts at 175.5° (corr.). The crystals deposited from alcohol have the composition—



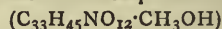
When dried at 100° they still retain one molecular proportion of water, which is, however, lost at 120°. The aqueous solution is laevorotatory: $[\alpha]_D = -7.71^\circ$. It combines with auric chloride, forming an aurichloride considerably more soluble than the corresponding aconitine salt.

Aconine was prepared from the pure chlorhydride by adding silver sulphate and subsequent treatment of the aconine sulphate with exactly sufficient baryta water. The solution on evaporation furnished a hygroscopic

brittle gum which refused to crystallise; this melted at 132° (corr.), and on analysis it afforded numbers agreeing with the formula $\text{C}_{26}\text{H}_{41}\text{NO}_{11}$, which is that proposed by Dunstan and Ince from the results of their study of pure aconitine. Aconine is very soluble in water; the aqueous solution is alkaline. When dry it is insoluble in ether and almost insoluble in chloroform. It is a powerful reducing agent, precipitating the metals from solutions of gold and silver salts; it also reduces Fehling's solution. The physiological action of pure aconine is being investigated. Its aqueous solution is slightly bitter and gives rise to a burning sensation in the mouth, but does not produce the tingling which is characteristic of aconitine. In respect of its action on polarised light aconine exhibits the same peculiarity as aconitine. Its salts are laevorotatory, whilst a solution of the alkaloid is dextrorotatory, $[\alpha]_D +23^\circ$. When heated with alkalis aconine slowly resinifies.

The examination of various agents on aconine has so far not led to any important results. Nitrous acid fails to attack it. The principal product of its oxidation by alkaline permanganate is oxalic acid. Attempts to isolate an additive compound with methyl iodide have been unsuccessful.

By the action of methyl iodide on aconitine a crystalline aconitine methiodide ($\text{C}_{33}\text{H}_{45}\text{NO}_{12} \cdot \text{CH}_3\text{I}$) was obtained, which melts at 219° (corr.). The aconitine methiodide prepared from the compound—



is amorphous, and the salts which it yields do not appear to crystallise. A further study will be made of this compound, and its physiological action will be investigated.

At the conclusion of the paper Professor Dunstan exhibited and described a simple laboratory shaking appliance devised by Mr. Dymond and himself, an account of which is to be found at p. 148.

DISCUSSION.

Mr. HOWARD said that the important conclusion now arrived at by the authors as to the nature of the alkaloids of pure *Aconitum napellus* illustrated the value of the botanist and chemist working together; it was to be expected that their co-operation would lead to other valuable results in the future, as the success achieved in increasing the yield of cinchona alkaloids would probably lead to progress being made in increasing the medicinal value of other plants.

Professor THORPE questioned the desirability of associating an old name with a new alkaloid.

The PRESIDENT expressed a similar opinion, citing the case of thiosulphate and hyposulphite in illustration of the confusion sometimes caused by such action.

Professor DUNSTAN, in his reply, said that the investigation had been made possible in the first instance only through the liberality of Mr. Howard, who gave them no less a quantity than an ounce of aconitine extracted by a known process from *A. napellus*. Napelline was a name which had been very little used, and it was very difficult to devise a better appellation for the new alkaloid.

*117. "Note on the Carbon Deposited from Coal-gas Flames." By WM. FOSTER, M.A.

The author quotes analyses of cokes obtained by carbonising sugar and starch:—

	Carbon.	Hydrogen.
Cane-sugar coke—high temperature	95.0	1.1
" " " " " " " " " " " "	94.1	1.2
Starch coke.. .. .	95.0	0.9

From the similarity in composition of these cokes to that of the soot obtainable from coal-gas flames, he is of opinion that there is a resemblance in the general character of the chemical processes whereby they are formed.

*118. "The Volumetric Estimation of Mercury." By CHAPMAN JONES.

The author has found the cyanide method of estimating

mercury suggested by Hannay (C. S. Journ., 1873, 565) and modified by Tuson and Neison (*ibid.*, 1877, xxxii., 679) to be unsatisfactory, the presence of carbon dioxide interfering with the titration. If, however, instead of adding the potassium cyanide solution until the turbidity produced by ammonia disappears, the titration be finished by adding, with certain precautions, a standard mercury solution until a definite and permanent turbidity is produced, concordant results are readily obtained. The method of working described is, if necessary, to separate the mercury as sulphide, and dissolve the washed precipitate in cold *aqua regia*, and to dilute and filter the solution. For the titration litmus extract is added and neutralisation effected with solid potassium carbonate and hydrogen chloride, and finally with dilute ammonia. Excess of the cyanide solution is added, then a slight excess of ammonia, and, lastly, a standard solution of mercuric chloride, until a permanent turbidity is obtained equal to that produced by 0.1 c.c. of the mercury solution in water containing about the same amounts of litmus and ammonia as the solution which is being titrated.

119. "Chromic Acid." By ELEANOR FIELD, Bathurst Student of Newnham College, Cambridge.

According to Moissan (*Ann. Chim. Phys.* [6], v., 568) it is possible to obtain crystals of the compound H_2CrO_4 by cooling with ice a solution saturated with CrO_3 at 90° . In the present notice results are quoted which show that the crystals obtained on following Moissan's directions are but those of CrO_3 .

The molecular weight of the dissolved substance calculated from the effect of CrO_3 on the boiling-point of water was found to be only 57, which is far below the theoretical value, viz., $CrO_3 = 100.4$. Ostwald, from determinations of the lowering of the freezing-point of water produced by CrO_3 , came to the conclusion that the aqueous solution contains $H_2Cr_2O_7$ dissociated into three ions: by trebling the mean value deduced from the boiling-point experiments, the value 171.85 is obtained, a number which does not agree either with the molecular weight of H_2CrO_4 (118.4) or with that of $H_2Cr_2O_7$ (218.8).

120. "The Origin of Acetylene in Flames." By Prof. V. B. LEWES.

The author has sought to determine whether acetylene is the product of high temperature change or of oxidation. The experiments described consisted in passing hydrocarbon gases and mixtures of such gases with others through a heated platinum tube 2 m.m. in diameter, which, judging from experiments made to test the point, would seem to be without special action.

On passing methane alone through the tube while a length of 6 inches was heated to 1100° in the flat flame of a broad Bunsen, a product was obtained containing 3.2 per cent of unsaturated hydrocarbons and 1.8 per cent of acetylene. The effect of heating methane with other gases is indicated by the following figures:—

	3 per cent oxygen.	15 per cent air.	50 p.c. carbon mon- oxide.	60 per cent hydrogen.
Unsaturated hydrocarbons	2.0	2.0	1.0	1.47
Acetylene	1.426	0.656	0.887	0.473
Carbon monoxide ..	1.1	1.0	—	0.490

These results appear to point to acetylene being formed by the action of heat alone.

Ethane heated alone gave a product containing 19.47 per cent unsaturated hydrocarbons and 3.224 per cent of acetylene. The effect of heating ethane diluted with 30 per cent of hydrogen with air was as follows:—

	15 p.c. air.	20 p.c. air.	25 p.c. air.
Unsaturated hydrocarbons	7.69	5.58	5.05
Acetylene	3.39	3.20	3.11
Carbon dioxide ..	0.00	1.01	1.51
" monoxide	1.54	2.53	3.03

The effect of temperature on the formation of acetylene is well shown by the following results obtained on con-

verting Russian petroleum into oil-gas in a Patterson retort:—

Temperature of retort ..	500°	700°	800°	900°
Yield of gas per gallon of oil	12 c.p.	60 c.p.	72 c.p.	84 c.p.
Illuminating power ..	54.8	50.7	57.1	42
Unsaturated hydrocarbons	39.13	36.56	36.55	22.04
Acetylene	0.052	0.084	0.38	0.46

Anniversary Meeting and Second Anniversary Dinner.

A letter in the following terms has been issued by the Secretaries to all Fellows on the Home list:—

"We have the honour to inform you that the Society's Second Anniversary Dinner is to take place at the Hôtel Métropole on Wednesday, March 30th, at seven for half-past seven o'clock, the Anniversary Meeting being appointed to take place at Burlington House at 4 o'clock in the afternoon of the same day.

"The price of the dinner, including wine, will be One Guinea, payable in advance.

"We beg to request that you will return the enclosed post-card duly filled in not later than March the 19th.

"A ticket admitting to the dinner will be sent to you on receipt of £1 1s., the price of the dinner ticket."

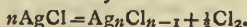
PHYSICAL SOCIETY.

March 11th, 1892.

Professor A. W. RÜCKER, F.R.S., Vice-President, in the Chair.

MR. H. M. ELDER, M.A., read a paper on "A Thermodynamical View of the Action of Light on Silver Chloride."

In the decomposition of silver chloride by light chlorine is given off, and a coloured solid body of unknown composition (sometimes called "photochloride") formed, the reaction being indicated by the formula—



If the experiment be carried out in a sealed vacuum the chloride is darkened up to a certain point, but regains whiteness when left in the dark. These facts have led the author to believe that the pressure of the liberated chlorine is a function of the illumination or intensity of light falling upon the chloride, in the same way as the pressure of a saturated vapour is a function of the temperature. Since illumination is a quantity in many respects analogous to temperature, he considers it not unreasonable to apply thermodynamic arguments, and regard chlorine, in presence of silver chloride and "photochloride," as the working substance in a "light engine." He therefore supposes a Carnot's cycle to be performed on the substances at constant temperature, the variables being pressure, volume, and illumination.

Since the cycle is strictly analogous to Carnot's, except that illumination is written for temperature, he infers that the efficiency is a function of the two illuminations. It also follows that just as Carnot's cycle is used to determine an absolute scale of temperature, so this cycle may be applied to determine an absolute scale of illumination. It only remains to determine an empiric scale analogous to the air thermometer, and to compare it with the photodynamic scale provided a method of making the comparison can be devised.

Assuming the axioms applied to Carnot's cycle are true when illumination is written for temperature, the author shows mathematically that $p \propto I^{\rho/T}$, where p is the pressure, I the illumination, T the absolute temperature, and ρ the heat of combination per grm.-molecule of chlorine evolved. If P be the heat of formation of silver chloride the fraction p/P may be considered as expressing the fraction of the total chlorine that can be removed by the action of light upon it, supposing the gas removed so as

to keep the pressure below that corresponding to the illumination. The chemical equation might then be written $P/\rho AgCl = Ag_{P/\rho} Cl_{P/\rho-1} + \frac{1}{2} Cl_2$; thus the formula for "photochloride" would be $Ag_{P/\rho} Cl_{P/\rho-1}$.

Prof. RÜCKER read a letter from the President (Prof. Fitzgerald) on the subject of the paper. He inquired what axiom corresponding with the second law of thermodynamics was employed. He was not sure that the engine was perfectly reversible, and felt doubt on the subject of phosphorescence mentioned in the last operation of the cycle. Nevertheless the paper was a most interesting one and very suggestive.

Prof. HERSCHEL pointed out that Becquerel's phosphoscope showed that all kind of light produced phosphorescence, and thought that in considering the subject, the non-thermal character of photogenic light should be kept in view.

Mr. BAKER said he had been working on silver chloride for several years, and found that no darkening whatever took place if kept dry *in vacuo*. He considered oxygen necessary to the action.

Dr. C. V. BURTON, referring to the motivity of the system, said that only a small fraction of the energy of the illumination was actually made use of. He also thought it necessary to consider how far the second law of thermodynamics could be treated as an axiom. He himself had been led to believe the law did not hold for mixtures of substances differing in a finite degree from one another. Some time ago he experimented on a solution of sodium sulphate placed in a dialyser and kept at constant temperature. The more acid portion passed through the membrane, and on mixing, a rise of temperature was observed; the dialyser thus acted like Maxwell's demons, and the mixing increased the motivity of the system.

Prof. RÜCKER expressed his doubts as to whether the cycle described in the paper was strictly analogous to that in Carnot's problem. In the latter case the parts of the working substance only differed infinitesimally from one another, whilst in the former the working body was a mixture of two solids and a gas. In order that the increased illumination should not alter the temperature, heat must be carried away. According to the paper the first part of the cycle must be both adiabatic and isothermal. This seemed hardly possible. If the chlorine alone be considered it could not be true, and it could only hold if the chloride absorbed all the heat given out by the compression of the chlorine. This seemed improbable, but if true it would be very important.

Capt. ABNEY saw another difficulty in the fact that at low temperatures silver chloride is not acted on, even by violet light, whereas heating greatly increases the action. In his opinion the conclusions arrived at required confirmation, but the paper would form a starting point for many new experiments.

Mr. ELDER, in reply to Prof. Fitzgerald, said the axiom corresponding to the second law, as stated by Clausius, might be formulated thus: Energy cannot of itself pass from a less bright to a brighter body. In the paper he had assumed that the energy given out during compression at the lower illumination was of the same quality as that absorbed at the higher. The whole question depended on comparisons of intensities of illuminations of different wave-lengths. In the expression $p \propto I^{1/T}$, p was probably a function of T , and Capt. Abney's objection was not necessarily fatal.

Speaking of the presence of oxygen being essential to decomposition, he believed some sensitising body was necessary, but judging from experiments he had seen an infinitesimal quantity would probably be sufficient, for the action seemed to be of a catalytic nature. He felt the weight of Prof. Rücker's objections, but thought they might possibly be met.

A paper on "Choking Coils" was read by Prof. PERRY, F.R.S. Regarding a choking coil as a transformer with

one primary and many secondaries, represented by the conducting masses, he pointed out that all the secondaries might be replaced by a single coil of n turns, and resistance r ohms, short-circuited on itself. Assuming no magnetic leakage the equations for the two circuits at any instant are $V = RC + N \theta I$ and $0 = rc + n \theta I$, where N and n are the turns, R and r the resistances, I the total induction in 10^8 C.G.S. lines, and C and c the primary and secondary currents respectively.

Since the exciting current C is all important in choking coils and its value depending on the law of magnetisation, the equations are treated in a different manner to that adopted in ordinary transformer calculations. Expressing the magnetic law as a Fourier series, $I = \sum A_i \rho_i \sin ix$, the value of A (viz., $NC + nc$) is deduced, and when V or I is given as a periodic function of the time, C may be calculated.

Assuming $V = V_0 \sin kt$, the author finds—

$$C = \frac{V_0}{N^2 \sigma k} \left[\sqrt{1 + 2e \sin f + e^2} \cdot \sin \{kt - 90 + \tan^{-1} \left(\tan f + \frac{e}{\cos f} \right)\} - b \cos 3kt - m \cos 5kt \right]$$

where $e = n^2 \rho k/r$, f is the hysteresis term, and b and m constants depending on the law of magnetisation. For ordinary transformer magnetisation $b = 0.2$ and $m = 0.05$.

From the above expression it will be seen that if there is no hysteresis (i.e., $f = 0$) the effect of the eddy currents, e , is to increase the amplitude of the important term and to produce a lead of $90^\circ - \cot^{-1} e$, whereas the effect of hysteresis without eddy currents is to leave the amplitude unaltered and produce a lead f . Putting $f = 0$ gives results in accordance with experimental observation; hence the author is inclined to believe that there is no hysteresis in transformers. He also points out that the higher harmonics must exist, and thinks it probable that a choking coil with finely divided iron may prove a method of increasing frequency by mere magnetic means.

Taking the case of a 1500 watt transformer (2000 volts) unloaded, in which the loss in eddies was 40 watts, it is shown that a secondary of 2 turns and resistance 1.9 ohms would replace the eddy current circuits. Assuming constant permeability and no eddy currents, the value of C comes out $0.07398 \sin (kt - 90^\circ)$, whilst with eddy currents and some saturation $C = 0.07911 \sin (kt - 69.2^\circ) - 0.014796 \cos 3kt - 0.003695 \cos 5kt$.

Dr. FLEMING said he was working on the subject of choking coils, and had found that in closed circuit transformers unloaded the real watts were about 0.7 times the apparent watts. This, on the assumption of sine functions, would indicate a lag of about 45° . A similar rule for open circuit transformers was much needed. It was important to know what size of core and coil was required to choke down to a given current.

Dr. SUMPNER thought it better to treat the subjects graphically rather than by analysis, and described a construction whereby the fundamental equations could be readily integrated.

Prof. PERRY said he had reason to think that ordinary hysteric curves were not applicable to transformers. By analysis of the experimental E.M.F. and current curves, one could work backwards and find the true hysteresis curves.

Synthesis of the Minerals Crocoite and Phornicochroite.—C. Ludeking.—These syntheses may be affected by exposing a solution of lead chromate in potassa to the air for some months in a flat-bottomed vessel. Sometimes a mixture of the two kinds of crystals is obtained. The composition of the crystals is the same as that of the natural minerals. Phornicochroite is obtained alone if the chromate is employed on employing the chromate with a large excess of concentrated potassa. If we use an excess of lead chromate along with potassium chromate crocoite is produced alone.—*Comptes Rendus*.

NOTICES OF BOOKS.

The Ilford Manual of Photography. By C. H. BOTHAMLEY, F.I.C., F.C.SS. (London and Berlin). Small 8vo., pp. 207. London: The Britannia Works Co., Ltd., Ilford.

THE standpoint of this manual is very clearly defined in the preface. It has been compiled for the benefit of the large number of photographers "who apply the art to pictorial, technical, or scientific purposes." Now, the wants of those who wish to photograph landscapes or to take portraits are very fully and ably met; but such as wish to apply photography to astronomical, meteorological, geological, or biological purposes, will here find little guidance. This we must regret to see, especially as the author is a master of the art of exposition. Those who are chiefly interested in the "experimental side of photography" are recommended to look elsewhere.

On the subject of shutters Mr. Bothamley is not very diffuse. For general purposes he recommends the Thornton-Pickard shutter, which he describes and figures. For very rapid exposure he admits that some special form of shutter is to be used, though he does not guide the tyro or the amateur in the difficult task of selection. "Difficult," we say, as a number of makers are each declaring that their especial devices are the best.

We are glad to see that the author cautions intrusive photographers—and we must confess that such persons exist—against surreptitiously introducing their "kodaks" or other detective hand-cameras into private premises. The most offensive of such Paul Pry's are those who try in this manner to take photographs of plant or machinery.

The chapter on photography by artificial light will be very useful in a climate like ours, where fog and cloud interfere so largely with natural light. The reader is warned that magnesium flash powders are in reality explosives, and must be dealt with as such. The precautions laid down by the author, if duly followed, will suffice to guard against any disastrous results.

Orthochromatic plates are recognised as highly useful, or rather indispensable, for photographing objects under the microscope. This information is about all which we have been able to find specially addressed to the microphotographer.

For the practical photographer who turns his attention to scenery or portraiture,—in other words to fully 90 per cent of the fraternity—this manual is highly to be recommended.

The Optical Lantern as an Aid in Teaching. By C. H. BOTHAMLEY, F.I.C., F.C.S. London: Hazell, Watson, and Viney, Ltd.

THE magic lantern, as it was called of yore, has in these days not merely undergone great improvements, but is being put to more dignified uses. The lantern as an auxiliary in school and college teaching is in many cases superseding the microscope, which can only be examined by one disciple at a time, and, except for geometrical diagrams, it must certainly consign the blackboard and chalk to oblivion.

Mr. Bothamley opens his subject with certain dry remarks on the system of instruction pursued until lately in ordinary schools. Of this kind of instruction he gives some striking examples. "Some of us have heard, too, of examinees in biology who had never looked through a microscope, and of so-called teachers of chemistry whose only apparatus was a blackboard and a piece of chalk." He does not add, as he might, that the "examinee in biology" passed, to the disgrace of the examiner, and of the entire educational system. Nor does Mr. Bothamley hint at the reason why mere verbalism, mere memory-work, has been so exclusively exalted.

An examiner can easily tell to what extent the memory

of a student has been cultivated, and how far it has been systematically directed to certain specified subjects. But to ascertain how far the youth has acquired the arts of acute and accurate observation, and of drawing right conclusions from the phenomena recognised, he is necessarily impotent. Hence, in countries where examinationism is rampant, education is made to consist more or less exclusively of mere memory-work; the physical and natural sciences are thrust into the background.

The old belief that the lantern can be successfully used only in a darkened room has been overturned by Mr. L. C. Miall, Professor of Biology at the Yorkshire College, Leeds. This is a great step in advance. We remember long years ago giving a lecture on the properties of phosphorus and its compounds before a promiscuous audience. The room was darkened whilst bubbles of hydrogen phosphide were allowed to ascend into a large glass receiver of oxygen gas. One of the lightning-like flashes revealed to the audience a boy in the act of very devoutly kissing a girl who was sitting close to him. We need scarcely say that this experiment very much interfered with the attention of the younger portion of the spectators.

Good instructions are here given for the position of the lecture-table, the lantern, and the screen. It is remarked that "at the Yorkshire College the number of slides required by the various departments is so large that the whole time of a special photographic assistant is occupied with their production."

Good practical instructions are here given on the manipulation of the lantern. The teachings of this little book are a not unimportant step in the much needed direction of school-reform.

CORRESPONDENCE.

LABORATORY STILLS.

To the Editor of the Chemical News.

SIR,—Will any of your readers kindly tell me the state of the law in relation to stills? I have a small still in use in my laboratory for distilling water, and am now informed by the Inland Revenue Office that I must pay a license for same, and am liable to an immense number of penalties for using same without express permission. As I never heard or dreamt that any license was required to distil water, I shall be glad to have further information on this subject. It seems that the law tries all it can to crush scientific progress in this country.—I am, &c.,

W. J. COOPER.

Detection of Saccharin.—D. Vital (*L'Orosi*).—The author proposes three methods. For this purpose the substance in question is mixed with three or four times its volume of slaked lime, and heated slowly to redness in a glass tube. There are obtained ammonia, calcium carbonate and sulphate, and phenol, which condenses in small drops in the cooler parts of the tube. The three former products are recognised by the usual methods. For the detection of phenol the author proposes the following reaction:—A few crystals of potassium chlorate are cautiously placed in a few c.c. of concentrated sulphuric acid; a drop of this solution is put in a porcelain capsule, and a glass rod moistened with the above-mentioned condensed product is plunged into it. There appears a green colouration which changes to an intense blue. The second method consists in treating the isolated saccharin with concentrated sulphuric acid. Benzoic acid is formed. The third method agrees with that of Schmitt and Pinette, who heat with caustic soda. The products are ammonia, salicylic acid, and sulphuric acid.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 10, March 7, 1892.

Fermentation of Blood.—MM. Berthelot and G. André.—The authors have operated upon a specimen of ox-blood, collected at the abattoir, and freed from fibrine. Its specific gravity at 15° was 1.045. Its fermentation lasted 130 days in a water-bath heated to 35°, and raised at the conclusion to 45°. The products are carbonic acid and ammonia, volatile fatty acids, and fixed nitrogenous principles. The carbonic acid was free from hydrogen and nitrogen, but contained traces of hydrogen sulphide and of ammonia. The proportion of ammonia formed is very considerable, two-thirds of the nitrogen of the albumenoid matters having been changed into ammonia by fermentation. The other third part of the nitrogen remains after fermentation in a fixed state. The fatty acids belonged exclusively to the series $C_nH_{2n}O_2$. The whole of the series was present from the formic to the caproic, and beyond. The fixed nitrogenous principles were resolved into four groups:—(1) an insoluble compound of a humic nature; (2) polynitrogenous acid forming soluble, crystalline barium salts; (3) a neutral or acid compound, soluble in absolute alcohol and non-crystalline; (4) alkaline salts, insoluble in alcohol.

Densities of Aqueous Solutions.—G. Charpy.—The contraction observed only in aqueous solutions corresponds either to a peculiarity in the constitution of the mol. of water, or to the existence in the midst of the solution or true chemical compound.

The Combinations of Gaseous Ammonia with Boron Bromide and Iodide.—A. Besson.—The bromine compound is a white amorphous body of the composition $BBr_{3.4}NH_3$. It is decomposed by water and by alkalis. The iodide is also a white amorphous solid, $BI_{3.5}NH_3$. It turns yellow on exposure to light, with the liberation of a small quantity of iodine. It is decomposed if heated in a current of hydrogen and is also decomposed by water.

Value of the Primary Alcohol Function.—M. de Forcrand.—A thermo-chemical paper, which does not admit of useful abstraction.

Transformation of Cupreine into Quinine Diiodomethylate.—E. Grimaux and A. Arnaud.—The authors, in reply to a memoir by Dr. Hesse in the *Annalen der Chemie*, October 15, 1891, maintain that the transformation is almost total.

Rapidity of the Decomposition of the Diazo-Compounds by Water.—P. Th. Müller and J. Hauser.—This decomposition is very slow at ordinary temperatures, but increases in rapidity with the rise of temperature. The rate of decomposition can be estimated by measuring the volumes of gas liberated.

Action of Capryl Iodide upon Trimethylamine in an Aqueous Solution in Equimolecular Proportion. Formation of Dimethylcaprylamine in Heat and of Caprylene in Cold.—H. and A. Malbot.—In heat we obtain four products: dimethylcaprylamine, tetramethylammonium iodide, trimethylamine hydriodate, and caprylene. In the cold we obtain merely the two latter products. In heat the most important product is dimethylcaprylamine, but in cold it is caprylene.

On Two Novel Species of Streptothrix and on the Place of this Genus in Classification.—C. Sauvageau and M. Radaes.—Cohn's *Cladothrix* is certainly a bacterium decidedly distinct from Cohn's *Streptothrix* and Harz's *Actinomyces*. The latter are hyphomycetes, which must both disappear as genera and be returned to Wallroth's genus *Oospora*.

MEETINGS FOR THE WEEK.

- MONDAY, 28th.—Medical, 8.30.
Society of Arts, 8. (Cantor Lectures). "Mine Surveying," by Bennett H. Brough, Assoc. R.S.M.
TUESDAY, 29th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.
Institute of Civil Engineers, 8.
Society of Arts, 8. "The Decorative Uses of Sculpture," by E. Roscoe Mullins.
WEDNESDAY, 30th.—Society of Arts, 8. "Foreign Exchange," by Ewing Matheson.
Chemical 4. (Anniversary). President's Address. Election of Office Bearers and Council.
THURSDAY, 31st.—Royal, 4.30.
Royal Society Club, 6.30.
Royal Institution, 3. "Epidemic Waves," by B. Arthur Whitelegge, M.D., B.Sc.
FRIDAY, April 1st.—Royal Institution, 9. "The Motion of the Ether near the Earth," by Prof. Oliver Lodge, F.R.S.
Geologists' Association, 8.
Quekett Club, 8.
SATURDAY, 2nd.—Royal Institution, 3. "Dramatic Music, from Shakspeare to Dryden," by Prof. J. F. Bridge, Mus. Doc.

ERRATA.—P. 144, col. 1, the composition of hæmocyanine should read as follows:— $C_{897}H_{1368}N_{223}CuS_4O_{258}$. In the paper on "Ptomaines" the formula for the alkaloid extracted from urine in cases of whooping-cough should be $C_8H_{10}NO_8$. And the sentence commencing "Afanassieff's, &c.," should read—"Afanassieff's bacillus gives rise to the same alkaloid as that extracted from urine in cases of whooping-cough."

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GUY'S HOSPITAL.

Entrance Scholarships for September, 1892.—Four Open Scholarships, two (125 guineas and 50 guineas) in Science, and two (100 guineas and 50 guineas) in Arts. Particulars and copies of examination papers on application to the DEAN, Guy's Hospital.

THE CHEMICAL NEWS.

VOL. LXV., No. 1688.

A "CHEMISTS' BENEVOLENT FUND."*

RESOLUTION of Council, passed November 19, 1891:—

"That a Committee be appointed to consider the letters from Prof. Attfield, of October 2 and November 16, 1891, relating to a Chemists' Benevolent Fund, and to report as to the course of action they deem most prudent for the Council to take with regard to the matter.

"That the Committee consist of:—Sir F. A. Abel, F.R.S., Prof. A. Crum-Brown, F.R.S., Dr. J. H. Gladstone, F.R.S., Dr. Hugo Müller, F.R.S., Prof. W. Odling, F.R.S., Dr. W. J. Russell, F.R.S., Prof. T. E. Thorpe, F.R.S., Prof. J. M. Thomson."

Report.

1. Your Committee beg to report that they have held four meetings on the subject, and have given careful consideration to the proposal for the foundation and administration by, or in connection with, the Chemical Society of a "Chemists' Benevolent Fund," as set forth in Prof. Attfield's letter of November 16, addressed to members of the Council, and more fully in his circular of October 2, 1891. Your Committee at one of their meetings had the advantage of Prof. Attfield's attendance, and have since been in further communication with him.

2. Your Committee, while sympathising with the general object sought to be attained, and making hearty acknowledgment of the zeal displayed by Prof. Attfield in the steps taken by him to initiate the proposed Fund, feel that they have been placed in a position of some difficulty by reason of the indefinite character of the particular proposal presented for their consideration.

3. In his letter of November 16, Prof. Attfield refers members of the Council to his circular of October 2, as "containing the conditions under which the contributions were obtained;" but neither from this circular nor from Prof. Attfield himself, by whom alone these conditions appear to have been propounded, have your Committee been able to ascertain which of the somewhat vaguely expressed conditions set forth in the circular are to be regarded as mere suggestions for the consideration of, and which as stipulations obligatory upon, the administrators of the proposed fund, in order to entitle them to the contributions so generously promised thereto.

4. So far as your Committee can gather, however, it was Prof. Attfield's intention to invite contributions to a Fund to be founded in celebration of the Jubilee of the Chemical Society, and to be dealt with as follows:—(1) "The supervision, at least, of both foundation and administration," to be undertaken by the Council of the Chemical Society. (2) The details of administration to be conducted by "a Board of Fellows (of the Society), so selected by the Council as to be representative of all classes of chemists." (3) The benefit not to be limited to investigators and exponents of chemical science, or to Fellows of the Society, but to be open to anyone of whom it could be said, "that he is *bona fide* a chemist and is in distress." (4) The main purpose to be "the permanent relief of distressed chemists or their widows," and its aim to be "to provide annual pensions . . . to approved applicants of a given age." (5) The selection from among these approved applicants to be "by votes (of subscribers), under which only the fittest for relief will be relieved,"—a mode represented to be the only practicable one for the distribution and sustentation of a competitive

pension fund, framed as contemplated, on the lines of the Benevolent Fund of the Pharmaceutical Society.

5. Your Committee have grave doubts whether such a system of competitive annuities, under which, on an annuity becoming publicly announced as vacant, the successful applicant would secure, it might be, an undue measure of relief, while other scarcely, if at all, less deserving applicants might receive no relief at all, is a judicious or even defensible system. They consider a far more desirable plan to be that of entrusting a select body of administrators to deal privately with every case as it is brought to their notice, either by pension or otherwise, according to the circumstances of the particular case; and as regards any surplus of yearly income, either to add it to the capital fund, or let it be available for the requirements of after years, so as to make provision against the occurrence of occasional cases of urgency.

6. But whatever may be thought of these alternative modes of administering a Benevolent Fund, and putting aside for the moment the question both of the advisability or otherwise of the institution by the Chemical Society of any Benevolent Fund at all, and of the legal difficulties which the institution of such a Fund would have to encounter, your Committee are unhesitatingly of opinion that the administration of any fund instituted by the Chemical Society ought to be wholly unfettered by conditions imposed from without, and be conducted solely according to regulations approved and authorised by the Society itself from time to time.

7. Your Committee, while recognising that, under the Charter of the Chemical Society, the creation or acceptance of a Benevolent Fund by the Society would be attended with serious difficulty, have little doubt but that if the institution of the Fund were felt to be eminently desirable, this difficulty might, in some way or other, be obviated or overcome. But taking into account all the circumstances, and especially the considerations stated below, they question very much whether the resulting advantages would not be more than counterbalanced by the disadvantages attendant on the institution and administration of any such Fund by the Society.

8. As sustaining their doubts on this point, your Committee feel that, to whatever extent Prof. Attfield's, or some other like, Fund is, or might be, intended to afford relief to persons whose claim would be based in any way on the contributions they had made to the advancement of chemical science, the necessities of such persons are met in very full measure by the Scientific Relief Fund of the Royal Society; and that, so far as this class of persons is concerned, the effect of the institution of a distinct Relief Fund by the Chemical Society would be, *pro tanto*, to liberate the existing Royal Society Fund from its present obligations towards necessitous scientific chemists and their families, and thereby to withhold from this class of persons in the future the ready and very liberal support from that Fund which has heretofore been accorded them.

9. On the other hand, as regards the large and often poorly remunerated class of persons whose claim to relief from the proposed new Fund would be based, not on their contributions to chemical science, but on the circumstance of their having been, in different grades, honourably and usefully engaged in the practice of professional chemistry, your Committee cannot but bear in mind that the Chemical Society, though founded mainly by professional chemists, was not founded for any professional object, but solely for the advancement of the science of chemistry; and that the Society, from its origin until the present day, while sympathising with the actively progressing development of professional chemistry, and with the measures taken of late for its better recognition, has consistently declined to regard the interest of professional chemists as one with which it was especially concerned, or for which it could accept any responsibility. This being so, it would, in the opinion of your Committee, be unwise for the Society to abandon, and to lay itself open to the imputation of

* Report of a Committee of the Council of the Chemical Society.

having been ready at once to abandon, its settled and well recognised policy, as soon as it became a question of acquiring funds for the Council of the Society to control and, directly or indirectly, administer.

10. Having regard to the objects for which the Chemical Society was instituted and incorporated, it is clear that the management of its affairs must be mainly in the hands of the most active and distinguished of the workers in chemical science; and it appears to your Committee that the privately conducted administration by the Council of the Society, or any delegacy appointed by, and responsible to, the so constituted Council, of a Fund to be shared in common by one set of persons whose claim would be based on their contributions to chemical science, and by another and larger set of persons whose claim would be based on their engagement in chemical practice, could scarcely fail to provoke a well-founded dissatisfaction among the latter class; while a resort to any form of popular election or control would as certainly be prejudicial to persons of the former class, whose interests the Chemical Society is more especially under obligation to shield and have regard for.

11. On these grounds then, namely, the sufficiency on the one hand of the continuously increasing Scientific Relief Fund of the Royal Society to meet the distresses of persons engaged in the advancement of chemical science, and the unfitness, on the other hand, of the Chemical Society to undertake the responsibility of providing for the distresses of persons engaged in chemical practice, as well as on the legal difficulty to be got over, and on yet other grounds, which, though felt to be of importance, it has not been thought necessary to dwell on, your Committee have reluctantly come to the conclusion that they cannot recommend the Council to undertake the charge with which it has been proposed to entrust them as representing the Chemical Society, of founding and administering a "Chemists' Benevolent Fund."

Signed on behalf of the Committee,

F. A. ABEL.

January 29, 1892.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 29TH, 1892.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, March 14th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 175 samples examined were found to be clear, bright, and efficiently filtered.

In other respects, also, the condition of the water supply during the month of February was throughout entirely satisfactory. In the case of the Lea-derived water supplied by the East London Company, the mean amount of organic carbon was found to be only 0.125 part, and the maximum amount 0.157 part in 100,000 parts of the water. In the case of the Thames-derived supply, the mean amount of organic carbon was only 0.137 part, and the maximum in any single sample examined 0.151 part in 100,000 parts of the water; as against a mean of 0.158 part, and maxima of 0.189 and 0.204 part in the previous month's supply.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg.

PAPER II.—Analyses of Raw Materials. Preparation of Crucibles.

THE following tables show that the Poutiloff Works were in a favourable position to start the crucible steel business:—

(a) Swedish Cast-iron.

	Per cent.
Carbon	3.800
Graphite	1.380
Manganese	1.040
Phosphorus	0.019
Silicon	0.728
Sulphur	0.025

(b) Swedish Iron, *γ*.M.

	Per cent.
Carbon	0.020
Graphite	none
Manganese	0.070
Phosphorus	0.014
Silicon	0.003
Sulphur	0.014

(c) Blister Steel, W.F.

No. I.

	Per cent.
Carbon (total) ..	1.200
Phosphorus	1.020
Sulphur	0.015

No. II.

Carbon (total) ..	1.050
Phosphorus	0.024
Sulphur	0.015

No. III.

Carbon (total) ..	0.850
Phosphorus	0.020
Sulphur	0.015

(d) Russian Puddled Steel.

No. I.

	Per cent.
Carbon (total) ..	0.370
Phosphorus	0.022
Silicon	0.110

No. II.

Carbon (total) ..	0.310
Phosphorus	0.046
Silicon	0.150

No. III.

Carbon (total) ..	0.255
Phosphorus	0.030
Silicon	0.150

The Russian puddled steel (Beloretz Works) contained only traces of sulphur and manganese. We classified the blister steel and the puddled as ordinarily by the aspect of the fracture.

(e) Siemens-Martin Steel.

Acid.

	Per cent.
Carbon	0.450
Manganese	0.985
Phosphorus	0.062
Sulphur	0.027

Basic.

Carbon	0.090
Manganese	0.440
Phosphorus	0.040
Sulphur	0.022

(f) Old Crucible Steel.

No. I.

	Per cent.
Carbon	0.958
Sulphur	0.068
Phosphorus	0.042

No. II. (mostly files).

Carbon	1.082
Sulphur	0.071
Phosphorus	0.075

(g) *Ferromanganese.*

	Per cent.
Carbon (total) ..	4.020
Manganese ..	74.710
Phosphorus ..	0.077
Sulphur ..	0.880

(h) *Silicon Pig-iron.*

	Per cent.
Carbon (total) ..	2.930
Manganese ..	14.940
Silicon ..	10.420

The silico-spiegel (h) contained 10 per cent of silicon and 20 per cent of manganese.

In some cases (casting ingots for tyres) we added a certain quantity of ferrochrome. Steels containing about 0.35 per cent of chromium have a greater tenacity.

Ferrochrome from Boucau (France).

	Per cent.
Chromium ..	49.25
Carbon (total) ..	9.03
Aluminium ..	2.28
Manganese ..	0.70
Silicon ..	0.62
Phosphorus ..	0.08
Sulphur ..	0.03

Several boxes contained 60 per cent of chromium; in this alloy 11.03 per cent of carbon (total) was found.

We prepared the crucibles out of Russian fire clay, coming from the Government of Novgorod. The price was 25 paper copecks, delivered at the Works. The only foreign material used in the manufacture of crucibles was the Ceylon graphite, costing here 5.50 paper roubles. It is impossible to use the Siberian graphite owing to the enormous amount of ash it contains. A certain quantity of fire-clay was roasted. All the materials were ground up. Each crucible weighed about 50—55 pounds. The composition of the mixture for the preparation of crucibles was as follows:—

Fire-clay ..	43.5
Burnt clay ..	36.5
Old crucibles ..	11.0
Graphite ..	9.0

The materials were mixed in a wooden tray lined with sheet iron by means of bare-footed workmen, who sprinkled the materials from time to time with water.

Composition of Raw Fire-clay.

Silica ..	50.00
Alumina ..	47.00
Magnesia ..	0.46
Lime (CaO) ..	0.52
Alkalies ..	0.71
Ferric oxide ..	2.05

This clay is of a good quality and very seldom contains pyrites, which are easily picked out before the grinding operation commences. The burnt clay is prepared in ordinary round brick furnaces.

The mass for crucibles, formed into rough blocks, is placed for a week into a cool place and next made into crucibles in hand-moulds by driving a pestle through the mass with a wooden mallet. Two men were employed (head workman receiving 12 copecks for each crucible, and paying himself his assistant). They made 65—70 crucibles per day. After remaining about a week in the moulding room, the crucibles were removed to the drying room, at a temperature of 40—45° C., where they remained for six to eight weeks.

The crucibles stood very fairly four heats while melting hard steel, and three heats for medium steel (tyres, steel castings, &c.). The whole cost of a crucible with the cover was 1.50 roubles to the Works themselves.

Royal Institution.—Dr. B. W. Richardson will deliver his Friday Evening Discourse on "The Physiology of Dreams" on the 29th of April in place of Dr. William Huggins, who will give his lecture on "The New Star in Auriga" on the 13th of May.

NEW SEPARATION OF ZINC AND MANGANESE.

By PAUL JANNASCH and ROB. NIEDERHOFHEIM.

RECENTLY one of the writers, in concert with J. Franzek, made known a new method for the separation of manganese, cobalt, and nickel, depending upon the precipitability of manganese from a basic potassic solution of the double cyanides of the metals concerned whilst cobalt and nickel remain in solution.

This process has now been applied with equal success to the separation of manganese and zinc. In absolute accuracy it is by no means inferior to the older process (precipitation of the manganese in a strong solution of ammonium chloride and ammonia), and is at once simple and expeditious in its performance.

0.5 gm. each of manganese and zinc sulphates are dissolved in 50 c.c. of water in a large platinum dish provided with a lip, and mixed with 10 c.c. of a 10 per cent solution of potassium cyanide, after which 10 c.c. of a 25 per cent potassa-lye are added, and the mixture is stirred with a platinum solution until the precipitate is almost entirely re-dissolved. The manganese is then precipitated with 50—60 c.c. of a pure solution of hydrogen peroxide, and the mixture (covered) is heated for 15—20 minutes upon a boiling water-bath, and then filtered into a second capacious platinum capsule and washed out with hot water. When the filtrate is quite cold it is supersaturated with hydrochloric acid (30 c.c. of the concentrated acid), and poured back into a capsule of Berlin porcelain (on account of the potassium nitrate often found in no small proportion in commercial hydrogen peroxide), evaporated to dryness, the residue heated in the air-bath to from 110°—115° for at least half an hour, re-dissolved in water with the addition of 15—20 drops of dilute hydrochloric acid, and separated by filtration from the deposit of silica which is rarely absent. Lastly, the filtrate whilst boiling is precipitated in the prescribed manner with sodium carbonate, and the zinc is subsequently weighed as oxide. The zinc oxide, after ignition, should give a clear solution in dilute acetic acid. An insoluble residue, if present, consists of silica or alumina or of both these impurities, the latter of which appears almost regularly,—often, indeed, in considerable quantities, if the alkaline solution, manganese hydroperoxide, has been heated for a long time on the water-bath, not in a capsule of platinum, but in a porcelain vessel. As a matter of course in this method of separation the use of impure reagents which contain alumina, silica, &c., is excluded. It must further be considered that the precipitate of manganese after washing with hot water, may easily include some potassa which cannot be readily removed by ignition with the blast. It is therefore prudent to re-dissolve the precipitate in dilute nitric acid in presence of a small quantity of oxalic acid (not more than 0.3 gm.), and to re-precipitate of the manganese with hydrogen peroxide in an ammoniacal solution.

The authors hope shortly to report on further quantitative determinations and separations by means of hydrogen peroxide. At present they are engaged upon the separations of copper and zinc, copper and nickel, lead and zinc, as also bismuth and zinc. The foundations of the methods have already been ascertained, and merely require a more minute elaboration.

In particular, as regards the behaviour of copper with hydrogen peroxide, it must be mentioned that slightly ammoniacal solutions of copper containing only small quantities of ammoniacal salts are completely precipitated by an excess of hydrogen peroxide, so that in the filtrates not the slightest trace of copper is indicated by hydrogen peroxide. These precipitates are of a dark greyish green, and retain their colour even after prolonged boiling.

The alkaline solutions of the double copper cyanides are also precipitated after prolonged boiling with hydrogen peroxide, whilst many other metals remain in solution.

The authors are now engaged with the study of these reactions so important for quantitative analysis.—*Ber. der Deutsch. Chem. Gesell.*, vol. xxiv., p. 3945.

THE CHEMICAL WORKS OF FARADAY IN RELATION TO MODERN SCIENCE.*

By Prof. DEWAR, M.A., F.R.S.

PROF. DEWAR commenced his lecture by saying that his eminent colleague had done such ample justice to the physical side of Faraday's work, that his own task would be limited to dealing with those early researches in which he developed that astounding manipulative power which enabled him to conduct his subsequent electrical investigations in so remarkable a manner. He proposed to give a brief sketch of the more important of the distinctive chemical labours of Faraday, and then to select one of the many veins of investigation he had opened up, and show what had resulted from its development.

Faraday's chemical work might be divided into the following groups or periods:—Period of Analytic Work. Organic Research. Study of Gaseous Properties. Investigations on Steel and Glass. Determination of Electro-chemical Equivalents. Regelation. Action of Metals on Light. Work on Chemical Manipulation. Published Lectures.

Having given a short résumé of Faraday's progress through these subjects, Prof. Dewar referred to his first great work in organic research, the production of two compounds of chlorine and carbon, the perchloride and the protochloride, and the determination of the composition of "Julian's chloride of carbon." The original specimens prepared by Faraday were exhibited, and it was pointed out that the discoverer's analyses of these bodies were absolutely accurate, notwithstanding the difficulties attending such work at that time. His discovery of "bicarburet of hydrogen" (now widely known and largely manufactured as benzol) and a "new hydrocarbon" (now known as butylene) was then described, it being pointed out that having regard to the methods of working which Faraday had to employ, the isolation and determination of the composition of such bodies was marvellous, and was to be explained only by his wonderful manipulative skill.

Probably Faraday's most remarkable discovery in organic chemistry was the fact that naphthalene could be dissolved by strong sulphuric acid, and that when thus dissolved the solution did not precipitate naphthalene on being treated with water. That enabled him to prove combination between sulphuric acid and a hydrocarbon. The body, which he called "sulpho-naphthalic acid," is probably the first of the sulpho-acids now so largely employed in the colour industry.

Faraday's next important work was an investigation into the properties of combinations of steel with other metals, in the course of which he demonstrated the now well-recognised fact that an admixture of such minute proportions as 1-500th of such metals as silver, nickel, palladium, &c., will entirely alter the character of the metal. Concurrently with this, he worked on the improvement of optical glass, and it was observed that although the fruits of his labours in this direction lay dormant for some time, they ultimately resulted in one of his most important discoveries, namely, the rotation of the plane of polarisation in the magnetic field. The glass produced by Faraday by the fusion of oxide of lead with boracic acid was selected by him because of its superior fluidity, combined with great density. (Experiments were given illustrating the peculiar physical and electrical properties of the Faraday glass).

The next research was that on the liquefaction of gases, which, although carried out by Faraday, was nevertheless done at the instigation of Davy. Davy had discovered a substance which proved to be a hydrate of chlorine, and which he found could be kept either in ice or in sealed tubes. Faraday had produced a quantity of this substance during the cold weather, and had made an analysis of it. Davy then suggested that it should be heated in a sealed tube, and, without saying what he really expected to take place, indicated that one of three things would happen, namely, that it would either melt, act on water, or produce liquid chlorine. The latter event happened, and opened up vast possibilities, the prosecution of which Davy left to Faraday. (Experiment on the liquefaction of chlorine given). The necessity of obtaining tubes strong enough to stand the pressure required for the liquefaction experiments led Faraday to make investigations at this time into the production of bottle and other glass.

Faraday next turned his attention to researches on the electro-chemical relations of bodies, crystallisation, and the action of metals on light. It was in connection with the research on crystallisation in 1856 that Faraday made his interesting discovery of the phenomenon of regelation, by virtue of which two portions of a piece of ice, after being severed, freeze together again on being brought into contact, even when the temperature of the surrounding medium is higher than the freezing-point of water. Although discovered by Faraday, it was not until comparatively recent times that the explanation of the phenomenon was given and its influence on glacial motion clearly established. (Experiment on regelation shown).

Specimens, arranged and tabulated by himself, of Faraday's last research on the optical properties of gold leaf in a highly attenuated form were exhibited and described.

Turning then to the special subject of the evening's discourse, the liquefaction of gases, Prof. Dewar stated that although Faraday made his first researches in this direction as early as 1823, the matter lay dormant for many years, until his interest in it was re-awakened by Thilorier's discovery that solid carbonic acid could be produced in the form of a snow-like substance, boiling at -80°C ., and capable of being handled. Faraday was the first to introduce this discovery into England in a lecture given at the Royal Institution on the 18th May, 1838, and thereafter by its aid he resumed his work on the liquefaction of the various gases which had resisted his former efforts. All through the summer of 1844 he was busily employed at this work, using the low temperatures, which Thilorier's new product enabled him to obtain, combined with great pressures. (Specimens of gases thus liquefied by Faraday shown). This important work was the subject of a Friday evening lecture given at the Royal Institution early in 1845, a full abstract of which appeared in the *Times* of that date, the Institution itself not having then commenced the publication of its proceedings. In the course of that Address Faraday produced a small quantity of ethylene, and he expressed the opinion that if a method could be found of producing liquid nitrous oxide in large quantities, that would be the material which would enable him to liquefy oxygen and the other gases which had hitherto resisted all his efforts. (Experiments showing the comparative boiling-points of solid carbonic acid, nitrous oxide, and ethylene at ordinary pressure and under diminished pressure given). Faraday hoped that the production of solid nitrous oxide would enable him to get temperatures as far below the boiling-point of carbonic acid as the temperature of that body was below ordinary temperatures. As a matter of fact, it is impossible to reach such low temperatures by the agency of solid nitrous oxide, and such great depression of temperature was not attained until such time as liquid ethylene became available. The lecturer here showed and described a diagram of the machinery and apparatus now employed at the Royal Institution for the liquefaction

* An Address delivered at the Faraday Centenary, Royal Institution of Great Britain, Friday, June 26, 1891.

and solidification of gases. The method of producing liquid ethylene and of employing it over and over again in the apparatus was described.

The work done in connection with this subject since the time of Faraday, and especially the investigations of Andrews and Van der Waals, had enabled scientists of the present day to calculate exactly the temperature of the boiling-point of hydrogen, the gaseous body which has in the liquid state the lowest boiling-point of all the elementary substances, and which has up to the present time resisted liquefaction. The temperature of boiling hydrogen would be -250°C . The lowest point attained by Faraday was 110°C ., and the lowest temperature yet reached was -210°C .

Prof. Dewar then performed the experiment of actually producing liquid oxygen, which was seen to boil quietly when collected in an open vessel at a temperature of -180°C . The colour was slightly blue, only a few particles of solid matter being visible, which Prof. Dewar explained were traces of solid carbonic acid, the elimination of which had given him considerable trouble. The lecturer further proved by actual experiment on his own hand and on a glass vessel that the liquid oxygen was in the spheroidal condition; and also that alcohol when added to the liquid became instantly solidified. The usual test for oxygen by means of a glowing taper was also made on the vapour given off by the liquid.

Prof. Dewar stated that the prosecution of the researches inaugurated by Faraday was enabling scientists to approach nearer and nearer to the zero of absolute temperature; and the speculations of physicists were now directed to the probable characteristics of hydrogen and of matter in general when that condition should be attained. At such a temperature the properties of matter would in all probability be entirely changed; the old Lucretian law would be suspended, molecular motion would probably cease, and what might be called the death of matter would ensue—as in fact the death of chemical affinity and chemical action was known to take place at the low temperatures already attainable. (Experiment proving this by the immersion of phosphorus, sodium, and potassium in liquid oxygen). On the other hand, it was found that even at such low temperatures oxygen retained its characteristic absorption spectrum.* Further experiments were given proving the liquefaction of ozone by means of liquid oxygen—a tube of the liquid thus produced showing the characteristic deep blue colour of that substance.

In conclusion, Prof. Dewar said that although great progress had been made since Faraday's time, chemists were still working distinctly on the lines of his early researches, and it seemed to him that no fitter method of celebrating the centenary of Faraday's birth could be chosen than the demonstration of the realisation of some of his own ideas.

On the conclusion of the lecture, a vote of thanks to Prof. Dewar was moved by the LORD CHANCELLOR, who said:—

* The recently discovered magnetic property of the liquid adds a new interest to this substance.

"Royal Institution, 10th December, 1891.

"DEAR SIR WILLIAM THOMSON.—The following observation, which I have just made, may interest the members of the Royal Society, and if you think it of sufficient importance you may announce it at this day's meeting.

"At 3 p.m. this afternoon I placed a quantity of liquid oxygen in the state of rapid ebullition in air (and therefore at a temperature of -181°C .) between the poles of the historic Faraday magnet, in a cup-shaped piece of rock salt (which I have found is not moistened by liquid oxygen, and therefore keeps it in the spheroidal state), and to my surprise I have witnessed the liquid oxygen, as soon as the magnet was stimulated, suddenly leap up to the poles and remain there permanently attached until it evaporated. To see liquid oxygen suddenly attracted by the magnet is a very beautiful confirmation of our knowledge of the properties of gaseous oxygen.—Yours faithfully, JAMES DEWAR."—*Proc. Roy. Soc.*, vol. i., p. 24.

My Lord Duke, my Lords, Ladies, and Gentlemen,—I am very happy indeed to be made the instrument of conveying your thanks for the most interesting lecture we have listened to. I could not help thinking while our lecturer was giving us an account of all these wonderful things, that he was illustrating in his own person something which he had said. He pointed out how the torch of science was passed on from hand to hand: how, for instance, Davy had handed to Faraday some of the sources of those great discoveries which he afterwards disclosed to the world; and I thought that it required some such successor to give adequate expression to the history of Faraday's work. Faraday had many friends; many of us have listened to him in this theatre, as, indeed, I have had the privilege of doing myself; and I think I may say that no one came within the sphere of his kindly and gentle influence who did not become a hearty and attached friend. But I should think that very few of those friends would be able to give adequate expression to what he had done, the discoveries he had made, and the ever increasing effect which those discoveries had exercised upon the progress of modern science. We have listened to-night to a most able exposition of Faraday's work, and I think that Prof. Dewar has shown that he has in truth succeeded to that work, that he is worthy to receive that torch, and carry it on and give a brighter illumination to science than it has ever yet received. I am sure that there is none here who will not heartily join with your Grace in thanking Prof. Dewar for the able, learned, and lucid lecture in which he has explained to ignorant people like myself Faraday's wonderful discoveries in science.

SIR LYON PLAYFAIR, in seconding the motion, said:—It is indeed a great privilege to all of us to see the great progress which has been made in the discoveries of Faraday during the last fifty years. Those little tubes containing the original liquefied gases which Faraday liquefied under pressure and low temperatures were very important, and were considered at the time very remarkable productions. But you see how the subject has since grown; how carbonic acid, for instance, first liquefied, has since been solidified so that it can be handled like snow; and you have seen the remarkable way in which oxygen has been liquefied on the present occasion. An old Professor of chemistry like myself can appreciate the wonderful manipulative power which Prof. Dewar has displayed this evening. Even in the chemical laboratory, with everything quiet around you, it is difficult to make these experiments successfully, but in a theatre of this kind it is marvellous how everything goes wrong; and if we had not had a manipulator of great accuracy and knowledge, we could not have had the gratification which we have enjoyed this evening. What strikes me as being so excellent in my friend, and much more than friend,—for he is the greatest chemist that I ever produced,—and I am extremely glad to think that he looks up to his old teacher with affection while I look to him with love and honour—what I wanted to say is, that I think he has done quite rightly in giving you the scientific side of these wonderful discoveries, and showing you the way in which they are growing and giving us a better knowledge of the condition of matter. When Faraday first made experiments like these, some wiseacres said, What is the use of it? Faraday replied, "Will you tell me what is the use of a baby?" But Faraday's baby has centred around it all the hopes and desires of the parents that produced it, and the State also has shown much interest in its upbringing. The bodies that appear in those tubes have become important factors in the progress and industry of the world. The carbonic acid, which I recollect first seeing as a little globe of acid, is now carried in cylinders filling railway trucks, and is applied to many purposes, some important, others more useful than important. For instance, the liquid carbonic acid enables barmaids to get beer up from the cellars below without pumping it; that nitrous oxide which we were so interested in as a con-

densed gas is now largely used by dentists as a means of extracting our teeth without pain; sulphurous acid will, I am certain, become most important in war, for if you took a brittle shell filled with liquid sulphurous acid and threw it between the decks of a ship it would produce such a stink that everybody would disappear in a moment. The time is coming when other gases will be used in this way. Their importance does not altogether consist in their applications to industry, though they are becoming very important in that way. But their importance is that they are teaching us more of the constitution and properties of matter; it is in that respect that they are becoming so interesting in the eyes of scientific men. I have been extremely interested in watching the production of that liquid oxygen. I looked upon it with great respect and wondered to see it not covered with a cage as if likely to go off at any moment in a terrific explosion. But it is produced in such a manner that its own cold keeps it down, and so we saw it handled in the most marvellous way as an ordinary liquid. I have the utmost pleasure in seconding the vote of thanks to Prof. Dewar for the brilliant exposition which he has given us.

The CHAIRMAN then put the motion, and it was carried with acclamation.

Prof. DEWAR, in reply, said: My Lord Duke, my Lords, Ladies, and Gentlemen,—I am exceedingly indebted to you for the very kind way in which you have referred to the labours of the lecturer. I can assure you that it has been a source of great pleasure to me, and that in fact I have had the least part to do. This kind of illustration cannot possibly be given without means of various kinds, and there are several benefactors whom I should like to mention in connection with this lecture. First of all, Dr. Anderson gave the pumps which enabled me to compress and evaporate such volatile bodies; secondly, we require machinery to set those pumps in motion, and somebody to look after it, and that has been supplied by the kindness of Mr. Robert Wilson, of the well-known firm of Messrs. Crossley, who is always ready and willing to help us; thirdly, as regards the cost of the material used—which has been by no means small—I am indebted to another member and great benefactor of the Institution, namely, Mr. Ludwig Mond, F.R.S. And lastly, but not least, I am indebted to my assistants, Mr. Lennox and Mr. Heath, for the assiduous and self-sacrificing way in which they have laboured in order to make these experiments go successfully. As Sir Lyon Playfair has said, it is comparatively easy to do these things in the quiet of the laboratory, but immensely difficult to get them to go on an occasion like this; and when we consider the long distances over which these highly condensed gases have to be conveyed, and the complex arrangements necessary to avoid all fear of danger, I think you will agree that the benefactors who rendered these arrangements possible are deserving of more credit than the lecturer.

Lord Justice FRY then proposed a vote of thanks to his Grace the Duke of Northumberland for his kindness in presiding over the meeting. In doing so his Lordship said: While I ask you to tender his Grace your hearty thanks for attending to-night, I cannot omit to ask you to thank him also for even greater services. He has presided over this Institution for many years, and has ever shown in its affairs a warm and intelligent interest, and he has been a most liberal benefactor of the Institution. At our ordinary meetings we have no opportunity of expressing our feelings to our benefactors, but on this extraordinary occasion we have that opportunity. I feel that I only express the sentiments of all here when I propose to proffer your warmest thanks to his Grace, not only for presiding this evening, but also for the great debt of gratitude which we owe him for his past services.

Sir RICHARD WEBSTER said: I have the great privilege of being permitted to second the vote of thanks to his Grace. I most heartily endorse all that Lord Justice Fry has said with respect to the eminent services rendered to

this Institution by his Grace the Chairman. I also heartily agree with what has been said by previous speakers with respect to the admirable lecture that we have heard to-night, some portion of which will, I hope, remain in my mind and memory, but the immediate effect of which has been to completely paralyse the power of ordinary speech. I feel it a great privilege to have been permitted to take some part in the proceedings, and have the greatest pleasure in seconding the vote proposed by Lord Justice Fry, which I venture to hope may be carried by acclamation.

The vote having been put and carried by acclamation, The DUKE OF NORTHUMBERLAND said in response: My Lords, Ladies, and Gentlemen, I feel somewhat embarrassed on the present occasion, because I had no expectation of, nor did I feel myself entitled to, the vote of thanks you have been so kind as to pass. I should have been wanting in duty if I had not been here to attend the Centenary of the illustrious man whose memory we have met to celebrate; and I must say I have been amply rewarded by the lectures I have heard, both from Lord Rayleigh and Prof. Dewar. They have almost persuaded me between them that I understand something of this science, which I confess but for them would have seemed impossible. Time is getting on, and I therefore will not detain you longer than to thank you most sincerely, and to ask you to accept this simple expression of my gratitude.

ON THE DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILISERS CONTAINING COTTON-SEED MEAL.*

By F. B. DANCY, A.B.

THE term *available* phosphoric acid is used to denote the difference between the *total* phosphoric acid in a fertiliser and the *insoluble*. The *total* phosphoric acid is the entire amount of phosphoric acid, of whatever kind, that the fertiliser contains. The *insoluble* phosphoric acid is, as generally accepted, that phosphoric acid which is left after 2 grms. of the fertiliser, ground to pass a sieve of approximately 20 meshes to the linear inch, have had the *soluble* phosphoric acid extracted with cold water and then been digested for thirty minutes, with agitation every five minutes, at 65° C., with 100 c.c. of a strictly neutral solution of ammonium citrate of a specific gravity of 1.09, immediately after which digestion they have been thoroughly washed with cold water.

The *available*, then, being the difference between the *total* and the *insoluble*, it follows that *insolubles* being equal, the *available* varies exactly and directly as the *total*, and *totals* being equal, the *available* varies exactly, though inversely, as the *insoluble*.

The *total* is a definite and fixed quantity, and there should, therefore, be no material variation in its determination between the work of accurate analysts. Not so with the others. The *soluble*, *insoluble*, *reverted*, and *available* are not fixed and definite quantities: they are dependent on so many conditions of time, temperature, degree of fineness, quality and quantity of solvent, agitation, &c., that it is no matter of wonder that even skilful manipulators vary in their determination. They are the results of methods, and will vary according to the method or manner of executing the details of the method. But, as has been remarked, and as its name implies, the *total* is all the phosphoric acid in the material under examination, of whatever kind and in whatever shape or form. It is not what is gotten by a method, but *what there is there*, and any method, therefore, that fails to reach any part or kind of it is not a method for *total* phosphoric acid. It is

* From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

sometimes said that discrimination is impracticable, and that all fertilisers should be treated equally and alike. The position is untenable. It might as well be urged that in order not to discriminate, the plain soda-lime method for the determination of nitrogen should be used on all fertilisers, those containing nitrates as well as those containing organic nitrogen alone, when everyone knows that it is inadequate in the presence of nitrates. So a *total* method which is adequate for some kinds of fertilisers, but not for others, cannot be applied to all on the above ground or any other ground without manifest injustice to those fertilisers for which the method is inadequate.

The Association of Official Agricultural Chemists in their official methods ("Bulletin 24, United States Department of Agriculture"), give three alternate methods of determining *total* phosphoric acid. There is no distinction made between them, no indication that either is better adapted than the other for any particular class of fertilisers. The presumption is that they are given as interchangeable and equally allowable for all classes of fertilisers at the pleasure or option of the operator. It is the purpose of this article to show that one of them at least is entirely inadequate for fertilisers that contain cotton-seed meal, and that any chemist who uses this method on such fertilisers is in almost certain danger of doing these fertilisers a great injustice. The method referred to is the second of the three given, namely, "Solution in 30 c.c. of concentrated nitric acid with a small quantity of hydrochloric acid." The writer has not extended his investigation, except imperfectly, to the other two methods. It is only with this one, as applied to cotton-seed fertilisers, that this article has to do.

Cotton-seed fertilisers are comparatively unknown in the North. It seems, therefore, that the Southern members of the Association of Official Agricultural Chemists could not have been very wide awake to the interests of a class of fertiliser manufacturers peculiar to their own section of country when they failed to have attached to this method, at the time when it was adopted by their association as one of three alternate methods, the limitation "not applicable to fertilisers containing cotton-seed meal."

Cotton-seed meal is readily and entirely soluble in either "nitric acid with a small quantity of hydrochloric acid" or in nitric acid alone. But such a solution does not give up its phosphoric acid to molybdic solution. It would appear that certain nitro-organic compounds are formed which prevent the phosphoric acid in the solution from being yielded up to the molybdic precipitant. Whether this is affected by in some way rendering the menstruum a solvent for the phospho-molybdate of ammonia that ought to be formed, or, by holding the phosphoric acid in check, thus preventing such a combination, is not clear. But the fact remains. The attention of the writer was first forcibly directed to it when a sample of cotton-seed meal was submitted to him for a determination of the *available* phosphoric acid it contained. A nitric acid solution of 2 grms. of it was made (using also a little hydrochloric acid), the solution being perfect, and a total phosphoric acid percentage of 0.51 found. A duplicate made in the same way yielded 0.54 per cent. Being convinced that there was much more phosphoric acid in the meal than this, and recalling that a short time previously a gentleman had remarked that a friend of his had found materially more phosphoric acid in the ash of cotton-seed meal than by acid solution, 2 grms. of the meal were ignited to perfect ash, the ash dissolved in acid, and a percentage of 3.24 of *total* phosphoric acid found; a duplicate in the same manner yielded 3.20, though in this case the incineration was not quite so perfect, a little char being left. The true per cent of *total* phosphoric acid in the meal then was 3.24. A solution of 2 grms. made by hydrochloric acid with chlorate of potash also failed by something more than half of getting the full amount. This yielded 1.45 per cent. Next 2 grms. of

the meal were taken, washed with cold water in exactly the same manner as when extracting *soluble* phosphoric acid from an ordinary fertiliser, then digested with citrate solution, and again washed exactly as is done in the determination of *insoluble* phosphoric acid. The residue was ignited and the phosphoric acid determined. It was found to be 0.24 per cent. So not only did a cotton-seed meal, which showed only half a per cent of *total* phosphoric acid to a nitric acid solution, contain in reality 3.2 per cent, but 3 per cent of this 3.2 per cent was *available* by the methods of analysis.

A cotton-seed meal fertiliser may easily contain one-third cotton-seed meal, and, if the meal had the composition of that examined above, would owe 1 per cent of its *available* phosphoric acid to the meal. If, therefore, such a fertiliser were to be analysed by the nitric acid method, it would theoretically show a shortage of nearly 1 per cent of *available* phosphoric acid (0.90 exactly). While none of the experiments herein given exhibit as great a disparity as this, some approximate it, and it is believed that a disparity fully equal to this is quite possible. Whether the entire disparity is always due to the retention of the phosphoric acid of the meal alone, or whether in some cases the meal, while holding some of the phosphoric acid of the phosphate in check gives up more of its own, or whether, in other cases, the phosphoric acid of the phosphate in precipitating carries more of the meal's phosphoric acid down with it than would otherwise go, and thus lessens the disparity, is not clear. I am inclined to think that new and fresh meal will exhibit this peculiarity in a greater degree than old meal, though of that I cannot speak definitely. However that may be, there seems to be not much doubt that the disparity will be greater or less according to various conditions not well understood, and may vary from a third or a half of a per cent to even as much as 1 per cent.

Six fertilisers containing cotton-seed meal were chosen. They were not laboratory mixtures, but bona fide commercial fertilisers on sale in North Carolina. They will be distinguished as 56, 76, 77, 78, 110, and 57. In each the phosphoric acid was determined by dissolving 2 grms. in nitric acid plus a little hydrochloric acid with protracted heating. This is designated in the table below as "acid solution." Then in each the phosphoric acid was determined by incinerating 2 grms. and dissolving the ash in nitric acid. This is designated in the table as "incineration." Following are the results:—

	Total phosphoric acid.					
	56.	76.	77.	78.	110.	57.
Incineration] ..	10.04	9.77	9.16	9.93	10.07	9.97
Acid solution ..	9.49	9.13	8.66	9.25	9.56	9.95
Difference ..	0.55	0.64	0.50	0.68	0.51	0.02

No. 57 was an old cotton-seed meal fertiliser that had been carried over from last season. The meal had completely changed colour to a dark brown, so that to the eye the fertiliser would never have been judged to be a cotton-seed fertiliser. In this one alone was there no difference in the results of the two methods.

(To be continued.)

Examination of the Air at Breweries, &c., for Micro-Organisms.—P. Lindner (*Wochenschrift für Brauerei*).—The author places in every part of the establishment which appears questionable three sterilised glass cylinders side by side, leaving them uncovered for one hour. At the end of this time the first cylinder is charged with sterilised wort, the second with wort-gelatin, and the third with meat-juice gelatin, using the requisite precautions. Each cylinder is then closed with sterilised tufts of wadding, and in the two last cylinders the gelatin is caused to congeal uniformly over the sides, as in Esmarch's tube-cultures. The tube-cultures are then examined in the usual manner.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 17th, 1892.

Dr. W. J. RUSSELL, F.R.S., Vice-President, in the Chair.

MESSRS. John C. Hewlett, William Pullinger, Edward C. Cyril Baly, and John C. Chorley were formally admitted Fellows of the Society.

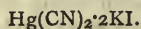
Certificates were read for the first time in favour of Messrs. Hudson Donaldson, Trevyr House, Grantham; Henry Leonard Humell, 15, Mawdsley Street, Bolton; Cresacre George Moor, B.A., St. Clement's Vicarage, Truro; John Meadows Smith, 66, College Street, Chelsea, S.W.; George de Roos Thompson, 28, Treleth Road, Askam-in-Furness, Lancashire; Arthur Holt Tuer, Thornhill, Wigan, Lancashire.

Of the following papers, those marked * were read :—

*121. "A Study of the Conditions which Determine Combination between the Cyanides of Zinc and Mercury; and of the Composition and Properties of the Resulting Double Salt." By WYNDHAM R. DUNSTAN.

When a solution of zinc sulphate is added to a solution of mercuric potassium cyanide $[\text{HgK}_2(\text{CN})_4]$, or when mercuric chloride is added to a solution of zinc potassium cyanide $[\text{ZnK}_2(\text{CN})_4]$, a white precipitate is formed which has been stated, on the authority of Gmelin, to consist of a double cyanide of zinc and mercury of the formula $\text{ZnHg}(\text{CN})_6$. This, the author has shown, is not the case (*Pharm. J.*, iii., 20, 653; *C.S. Abstr.*, 1890, 855). The precipitate loses a large quantity of mercuric cyanide when it is washed with cold water, some, however, remaining attached to the cyanide of zinc. Previous experiments seemed to point to the conclusion that the mercuric cyanide thus retained is not combined, but in some manner mechanically entangled by the zinc cyanide. This view is, however, disposed of by further experiments, of which an account is now given.

The precipitate is in many respects a remarkable substance. The amount of mercuric cyanide "retained" is dependent on the amount of water present during precipitation, as well as on the proportion in which the salts interact; the maximum quantity retained is 38.5 per cent. Zinc cyanide having this percentage of mercuric cyanide attached to it in such a form that it cannot be removed by ordinary washing with cold water is precipitated when cold saturated solutions of the two salts are mixed in equimolecular proportions. The washed precipitate is amorphous. Prolonged contact with cold water leads to the gradual removal of mercuric cyanide. Boiling water dissolves the mercuric salt more rapidly. A cold solution of potassium iodide readily dissolves the mercuric cyanide with the formation of the soluble double salt—



A series of experiments in which the masses of the interacting salts were varied proved that a compound of the two cyanides is formed, and suffers decomposition to a greater or less extent, depending on the relative amount of water present. An examination of the curves plotted from these results leads to the inference that the composition of the double salt is expressed by the formula $\text{Zn}_4\text{Hg}(\text{CN})_{10}$, that is to say, the two cyanides are present in it in the proportion $\text{Zn}(\text{CN})_2, \frac{1}{4}\text{Hg}(\text{CN})_2$. Such a salt contains 40.6 per cent of mercuric cyanide. It cannot be obtained pure, since it is decomposed by water, and it can only be produced by precipitation of aqueous solutions. Under the most favourable circumstances, when the quantity of water present is reduced to a minimum, a substance containing 98 per cent of the double cyanide is obtained; the remaining 2 per cent consists of zinc cyanide, resulting from the decomposition of some of the double salt by

water, the mercuric cyanide being dissolved, whilst the insoluble zinc cyanide remains mixed with the double salt. All attempts to prepare the double cyanide by other methods than that of precipitation have failed. Fundamental molecules of zinc cyanide and mercuric cyanide must apparently be present, in order that combination may occur. The aggregates of fundamental molecules $[\text{Zn}(\text{CN})_2]_n$ and $[\text{Hg}(\text{CN})_2]_n$, which constitute the solid salts, show no tendency to combine. No evidence is forthcoming of the existence of any other compound of the two cyanides than that now described. No similar compound of zinc cyanide with other metallic cyanides than that of mercury could be obtained.

This tetrazincic monomercuridecyanide, mixed with more or less zinc cyanide, has been found by Sir Joseph Lister to be an admirable surgical antiseptic, and it is at his suggestion that the enquiry was undertaken.

A full account of the best method of preparing the salt is given in the author's previous paper.

DISCUSSION.

Sir JOSEPH LISTER said that the great value of the salt arose from the circumstance that while equally effective as an antiseptic, it had none of the irritant qualities of mercuric cyanide; and its slight solubility was an advantage. When mercuric chloride was used, it was liable, on the one hand, to be washed away by the discharges, and, on the other, to accumulate until a solution was formed which was so concentrated that it caused great irritation.

*122. "A Lecture Experiment to Illustrate the Phenomena of Coal Dust Explosions." By T. E. THORPE, F.R.S.

The author describes an apparatus by which the phenomena of a coal dust explosion, resulting either from a local explosion of fire-damp or by the direct action of a blown-out shot, may be illustrated. For class-room demonstration he recommends the substitution of lycopodium powder for the coal dust, on account of the greater ease and certainty of the experiment, and also because its use allows of the observation of certain phenomena, such as the mode in which the dust which escapes complete combustion is thrown on projecting objects, and also the fact that the explosion gathers strength as it progresses, which is made evident by the gradually increasing area of clear space before such objects as the dust is swept away by the force of the explosive flame.

By observations made by means of a List manometer with this apparatus, he finds that there is no evidence of a diminution of pressure along the sides of the space through which the flame rushes, and he is of opinion that there is no experimental proof of the validity of the "suction theory" held by certain colliery managers, which assumes that in consequence of this alleged diminution of pressure occluded fire-damp is drawn out from the coal, and contributes to the violence of the explosion.

DISCUSSION.

Mr. HOWARD referred to two cases of "dust" explosions within his experience: one had occurred in a mill in which cinchona bark, a by no means inflammable substance, was ground; in the other case, soot produced by the burning of camphor had exploded after the fire itself had been put out.

Professor THORPE, in reply to a question of Mr. Bevan, said that although the explosion of coal dust was doubtless influenced by its composition, the condition of the dust appeared to be the more important factor. Mr. Newth had found that charcoal powder would explode.

*123. "The Production of the Ketone 1:2:4-Acetyl-ortho-xylene from Camphor by the Action of Sulphuric Acid and Zinc Chloride." By HENRY E. ARMSTRONG and F. STANLEY KIPPING.

In a recent communication (*Proc. C.S.*, 1891, 188) the authors stated that they had separated from the crude

product of the action of sulphuric acid on camphor a ketone of the formula $C_9H_{12}O$, mentioning that the results obtained on analysing its hydroxime were unsatisfactory; subsequent analyses of the hydroxime and several other derivatives of the ketone have, however, all given results confirming the formula $C_9H_{12}O$.

On treatment with bromine, the ketone yields an unstable bromide which readily decomposes, yielding the monobromo-derivative, $C_9H_{11}BrO$; this latter crystallises from petroleum spirit in colourless lustrous flakes melting at $63-64^\circ$.

On oxidation with dilute nitric acid, the ketone yields two acids separable by means of chloroform. One of these proves to be paraxylic acid, i.e., 1:2:4-dimethylbenzoic acid; the other being xylylidic, or 1:2:4-methylisophthalic acid. The formation of these two acids served to show that the ketone is 1:2:4-acetylorthoxylene, a compound which had already been prepared synthetically by Claus by the interaction of acetic chloride and orthoxylene in presence of aluminium chloride. The description of his product given by Claus was found to be substantially applicable to the product from camphor, but all doubt was set at rest by a direct comparison of the ketone prepared in accordance with Claus's directions with that obtained from camphor.

The theoretical bearing of this result will be fully discussed in the complete paper.

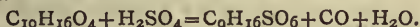
The authors are still engaged in examining the crude product contained in the ketone, in order to ascertain the nature of the constituent which communicates to it the characteristic strong peppermint-like odour which it possesses, and which appears not to be exhibited by pure acetylorthoxylene.

*124. "Platinum Tetrachloride." By W. PULLINGER, B.A.

The author has obtained this substance by heating hydrated hydrogen platinum chloride in a current of dry hydrogen chloride at 165° during fifteen hours. When thus prepared, it is a very soluble, but not deliquescent, substance.

125. "Note on a New Acid from Camphoric Acid." By W. H. PERKIN, jun., Ph.D., F.R.S.

When warmed with sulphuric acid at 65° , camphoric acid is converted into sulphocamphoric acid with loss of water and carbon monoxide:—



This remarkable decomposition was first examined by Walter (*Ann. Chim. Phys.* [3], ix., 177); subsequently by Kachler (*Annalen*, clxix., 183), and by Zepharovich (*Fahr.*, 1877, 641). Kachler showed that, when fused with potash, sulphocamphoric acid yields a crystalline substance, $C_9H_{12}O_2$ (m. p. 148°), which, although soluble in alkalis, is apparently not an acid.

In repeating Kachler's experiments, the author sulphated camphoric acid at 100° , and fused the resulting sulphonic acid with potash, according to Kachler's directions. The resulting product was distilled under reduced pressure, and the distillate, which on cooling completely solidified, was purified by means of baryta water, and subsequent re-crystallisation from dilute acetic acid. It was thus obtained in the form of beautiful glistening prisms which melt at 108° and sublime readily at 100° . The analysis gave the following numbers:—

	Theory, $C_9H_{12}O_2$. Per cent.	Found. Per cent.
C	71.0	70.7
H	7.9	8.1

This compound, which is isomeric with that described by Kachler, is a well characterised monobasic acid. The silver salt, $C_9H_{11}AgO_2$, was obtained on adding silver nitrate to a neutral solution of the ammonium salt as a white crystalline precipitate, which, on analysis, gave the following numbers:—

	Theory, $C_9H_{11}AgO_2$. Per cent.	Found. Per cent.
C	41.7	41.5
H	4.3	4.4
Ag	41.7	41.8

From these results it would appear that the acid obtained by sulphating camphoric acid at 100° is isomeric with ordinary sulphocamphoric acid. The author is engaged in an experimental comparison of these sulphoacids, and also with a detailed investigation of the new acid and of Kachler's isomeric compound.

126. "The Specific Rotatory and Cupric Reducing Power of Invert Sugar and of Dextrose obtained from Cane Sugar by means of Invertase." By JAMES O'SULLIVAN.

After referring to the various values assigned to the rotatory power of lævulose and to the doubt thrown on Dubrunfaut's value by the statements of Herzfeld, Bornstein, and Winter, the author minutely describes experiments in which hydrolysis of cane sugar was effected by invertase instead of by means of acid. The conclusion finally arrived at is that, as the specific rotatory power of invert sugar obtained by means of invertase, which has no action on lævulose, is $[\alpha]_D = -24.5$, and that of the dextrose prepared from such invert sugar is $[\alpha]_D = 57^\circ$, the apparent specific rotatory power of lævulose calculated from these numbers must be—

$$-24.5 \times 2 + 57^\circ = [\alpha]_D - 106$$

or $[\alpha]_D = 93.8$, a value agreeing with that generally accepted.

127. "Ethyldimethylamidobenzene." By W. R. HODGKINSON and LEONHARD LIMPACH.

The authors have prepared this amine by heating paraxyldine chlorhydride with ethylic alcohol under pressure at $250-300^\circ$; the product also contains diethyldimethylamidobenzene. The purification was effected by converting the mixture into sulphates; after re-crystallising the difficultly soluble sulphate of the ethyldimethylamine, the formyl compound was prepared and crystallised from weak alcohol.

The pure amine boils at 247° ; its formyl derivative crystallises in long silky needles melting at $104-105^\circ$; its acetyl derivative forms brilliant prisms melting at $142-143^\circ$.

128. "Action of Nitric Acid on Oxanilide and its Analogues." By A. G. PERKIN.

Although acetanilide and similar compounds are readily converted into mononitro-derivatives, the preparation of dinitro-compounds from them is often attended with difficulty, and trinitranilide has not hitherto been obtained directly from aniline or its derivatives. The author finds that oxanilide and its analogues are readily converted by nitration into the higher nitro-derivatives.

An improved method of preparing oxanilide and similar compounds is described, consisting in adding the oxalate of the amine to boiling coal tar cresylic acid and boiling the saturated solution for a few minutes.

The preparation and properties of the following substances are described:—

Tetra- and hexa-nitroxanilide.
Di- and tetra-nitroxalorthotoluide.
Tetranitroxalparatoluide.
Dinitroxal- β -naphthylide.
Tetranitroxal- α -naphthylcarbamide.

"Mono-, di-, and tri-nitroxanilic acids.

Higher derivatives of the toluides could not be obtained; the naphthylcarbamide derivatives were obtained as products of the continued action of nitric acid on the dinitroxalnaphthylides.

At the next meeting, on April 7th, the following papers will be read:—

"Platinous Chloride and its Use as a Source of Chlorine." By W. A. Shenstone and C. R. Beck.

"The Action of Silicon Tetrachloride on Substituted Phenylamines." By Professor Emerson Reynolds, F.R.S.

NOTICES OF BOOKS.

The Tannins. A Monograph of the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents. With an Index to the Literature of the Subject. By HENRY TRIMBLE, Ph.M., Volume I. Philadelphia: J. B. Lippincott Co., 8vo., pp. 165.

We have here the first volume of a monograph of a very complex and important department of vegetable chemistry. The author begins with an account of the early recognition of tannin as a distinct proximate principle, which he traces to the last ten years of the Eighteenth Century. Of course, astringents had been used in the arts from prehistoric ages, but without any inquiry as to their active principle. He uses the term tannin to include the whole class of astringents, and restricts the name tannic acid to the product from galls when purified.

The classification of tannins according as they form green or blue precipitates with the salts of iron is justly rejected by Mr. Trimble, since free acids, especially the tartaric, determine the green colouration, whilst, on the other hand, a cautious addition of an alkali changes the "greening" to the "blueing" tannins. As a more scientific classification he gives that proposed by Wagner, who divides tannins into the *pathological*, those produced in plants by the sting of an insect, and the *physiological*, which is generated normally in the tissues of plants.

The various methods devised for the determination of tannin are described, and the preference is awarded to that of Loewenthal, which is, however, recognised as by no means perfect.

The author concludes that tannic acid as we know it is either a glucoside of digallic acid or a mixture of this glucoside with variable proportions of digallic acid.

There is a very elaborate bibliography of the tannins which will be very useful to those studying this subject, but which we think might have been more appropriately placed in the promised second volume, after the description of the numerous astringent plants. This bibliography briefly mentions a paper on "Animal Tannin," by M. Villon, *CHEMICAL NEWS*, vol. lvi. This chemist obtained a modification of tannin from a corn-weevil. In the *Transactions of the London Entomological Society* for 1887, Mr. J. W. Slater shows the presence of tannin in a number of beetles which feed on vegetable matter.

We shall welcome the appearance of the concluding volume of Mr. Trimble's work.

Outlines of Theoretical Chemistry. By LOTHAR MEYER, Professor of Chemistry in the University of Tübingen. Translated by P. PHILLIPS BEDSON, D.Sc., F.C.S., and W. CARLETON WILLIAMS, B.Sc., F.C.S. With a Preface by the Author. 8vo., pp. 220. London: Longmans, Green, and Co.

THIS work belongs to a class which is at once useful and not overcrowded. The author tells us in the special preface which he has supplied for the English edition that he has written not for students alone, but has "been desirous of offering something to those friends of scientific investigation who have neither the intention nor the time to concern themselves with the details of chemical investigation, but wish to become acquainted with the general conclusions arrived at."

In other words, he endeavours to show as far as possible the complete building without obtruding the

ladders and the scaffolding upon our view. This is certainly at once the most pleasing and the most rational way of expounding the truths of chemistry to the non-specialist.

In accordance with this principle Professor L. Meyer expounds the leading conclusions of chemical science as at present recognised in a series of 123 sections, clearly written and judiciously arranged.

Concerning the capital question of the nature of the elements the author considers it improbable that they are really "primal forms of matter." He thinks that they will prove to be "combinations of units of a higher order." Prout's hypothesis he considers opposed to the best atomic weight determinations of Berzelius, Marignac, and Stas. This assertion cannot be contradicted. At the same time it might not have been useless to call attention to the fact that the atomic weights as actually determined approach in many cases curiously near to the values which they ought to present according to Prout's hypothesis. This question, however, concerns the investigating specialist much more than the general reader.

No more striking instance can be given of the development of chemical science during the past fifty years than the disappearance of speculations on the nature and the cause of "affinity," which is now pronounced of little or no use in explaining chemical phenomena. To the numerous class of persons for whom this work has been more especially written it must be pronounced invaluable.

A Dictionary of the Coal-Tar Colours. Compiled by GEORGE H. HURST, F.C.S., Member of the Society of Chemical Industry. London: Heywood and Co., Ltd.

THIS is a work which was very much needed. The coal-tar colours are so many in number, and they have received from patentees and manufacturers such a number of synonyms,—often very inappropriate,—that both the student and the practical dyer have often been no little perplexed. It may be necessary to explain what we mean by inappropriate names.

As a striking instance we may point out Indian yellow. This name has long ago been used as a synonym for *purree*, but now it has been seized upon by a German firm and applied to the colour better known as "azo-yellow" or "azo-acid yellow." Harmaline, which properly pertains to a proximate principle extracted from *Peganon harmala*, has been applied to an impure magenta.

Other objectionable names are phloxine, fuchsine, roseine, cyclamine, and many others which might lead to the mistaken impression that they were vegetable proximate principles.

As instances of names which cannot occasion any such confusion may be mentioned Titan brown, orange, and pink, Stanley red, the Gambines, the azines, and many others. This confusion, however, is not in any way due to the author. His task has been not to reform but simply to explain the existing nomenclature.

We have not detected in the work anything which can be considered an error. A few artificial colours are omitted, but they are such as have been superseded or have never come into industrial use at all. Such are benzoil blue (a mere mixture), isopurpuric acid, aveline, &c. Canarine, it might be objected, is not a coal-tar colour at all. But this frivolous complaint might have been at once excluded if the work had been entitled "Dictionary of the Artificial Colours." The introduction and the general remarks on dyeing and printing are ably and judiciously written.

It might save much trouble if the British Patent Office were authorised to reject specifications of the class which we have pronounced to be inappropriately named.

We consider that Mr. Hurst by compiling this work has conferred a very great benefit upon the tinctorial industries of this country, and we trust that it will find a place at every dye and print-works.

A Short Text-Book of Inorganic Chemistry. By Dr. HERMANN KOLBE, late Professor of Chemistry in the University of Leipzig. Translated and Edited by T. S. HUMPIDGE, Ph.D., B.Sc., late Professor of Chemistry in the University College of Wales, Aberystwyth. With a Coloured Table of Spectra and numerous Wood-Engravings. Third Edition, revised by H. LLOYD SNAPE, Ph.D., D.Sc., Professor of Chemistry in the University College of Wales. London: Longmans, Green, and Co. 8vo., pp. 616.

We have long regarded Kolbe's "Inorganic Chemistry" as one of the very best text-books which can be put in the hands of a student, and we are not surprised that even in this land of chemical manuals a third edition is already found needful. In Dr. Humpidge's preface,—which is here reproduced,—we notice, not without regret, the utterance that "in adapting the book for English students certain alterations and additions were necessary." It might have been well if these "alterations and additions" had either been given in the form of notes or had been marked out in the text by the use of distinct type. Readers who, like ourselves, have cherished the belief that science is the same in all countries, must naturally feel curious to know wherefore and in how far they have been mistaken? Certainly the final sentence of the preface throws some light on this point. The German original was written to meet the requirements of students who are working to *know*, and to add to the sum total of our chemical knowledge. But in the English version the "needs of students working for examinations have been steadily kept in view."

The appendix and the notes which have been supplied by the editor for the purpose of keeping the work on a level with the present state of knowledge are judicious and useful.

Two curious facts here mentioned (p. 134) should stimulate further research,—the failure of experimentalists to obtain hitherto a carbon fluoride and a fluorine oxide. We thoroughly approve of the recommendation that for the detection of arsenic in chemico-legal cases magnesium should be used in the Marsh process in the place of zinc.

CORRESPONDENCE.

LABORATORY STILLS.

To the Editor of the Chemical News.

SIR,—In reply to Mr. W. J. Cooper I may venture to assert that the law regarding stills was never meant to apply to those in use in private laboratories or chemical factories. I was recently engaged in a case (*Regina v. Illingworth*) in which it was successfully contended by the defendant's solicitor that the intention of the Act is to prevent the manufacture of liquors which are illicit, and surely distilled water is not one of them! In the case mentioned the Revenue people were attempting to impose a licence on a manufacturer who used a sulphate of ammonia still. The Bench of West Riding magistrates decided that "this still is not within the meaning of the Act." An appeal to a higher Court fell through on account of the death of the defendant.—I am, &c.,

WM. ACKROYD.

Borough Laboratory, Halifax,
March 28, 1892.

LABORATORY STILLS.

To the Editor of the Chemical News.

SIR,—Your correspondent, W. J. Cooper, has legally incurred a fine through having a still on his premises without either having paid for a license or having received permission from the Board of Inland Revenue to use the

same. He must address his request to the Commissioner of Inland Revenue, Somerset House, London, showing clearly that the still is used by him for chemical research.

The Board of Inland Revenue are very ready to allow stills free of excise license when it is proved beyond a doubt that they are wanted purely for scientific purposes, but *they must be asked permission* first. They have in the last few months also, to our certain knowledge, given permission to several directors of laboratories to obtain unmineralised methylated spirit.

We have had no case of the kind refused, and have forwarded several applications on behalf of the heads of laboratories to them. They are not so black as they are painted, but it must be made clear to them that stills are not wanted to manufacture articles for wholesale or retail sale, and that unmineralised methylated spirit is not required to sell, or by a party who also gets the mineralised article, as if this be the case they have to be stricter to protect their revenue.—We are, &c.,

A. and J. WARREN,
Wholesale Druggists and Licensed
Makers of Methylated Spirit.

23 and 24, Redcliff Street, Bristol,
March 28, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 11, March 14, 1892.

Researches on Samarium.—Lecoq de Boisbaudran.—The author has had placed at his disposal by Professor Clève about 3 grms. of the best samaria which he has ever possessed, and which he has fractionated with ammonia, but without obtaining the distinct separations hoped for.

On Certain very Definite Alloys of Sodium.—M. Joannis.—The author has obtained the compound, $\text{Pb 81.62, Na 18.38}$ per cent, contaminated, however, with a sodium amidide. On exposure to the air this compound heats strongly and in contact with water is decomposed, leaving soda and lead in the form of black flocks. The alloy of lead potassium, Pb_2K , is obtained by the action of an excess of potassium upon lead. Bismuth-sodium alloy, BiNa_3 , is obtained in an analogous manner. It ignites spontaneously in the air, throwing up a splendid sheaf of sparks. It is decomposed by water with an escape of pure hydrogen. Antimony-sodium alloy, SbNa_3 , is obtained in a similar manner. It ignites on exposure to air, and is decomposed by water with an escape of pure hydrogen.

The Assay of Antimony Ores.—Ad. Carnot.—This paper will be inserted in full.

The Vegetation of the Vine.—L. Ross and E. Thomas.—The saccharose formed during the ten or twelve first weeks of vegetation disappears in the leaves, the shoots, and even in the grapes, in the fourth month of vegetation. They then contain a mixture of sugars in which dextrose predominates. It is not always true to say that the acidity of fruits decreases as they approach maturity. The decrease of acidity in absolute value is observed at the moment when the levulose is decidedly increasing in the fruit. The polarimetric deviation passes to the left and increases progressively up to ripeness, when it is approximately equal to that of invert sugar.

Citric or Oxycarballylic Acid.—G. Massol.—In this thermo-chemical paper the author concludes that the formation-heat of potassium and sodium citrates in the

solid state is greater than that of the corresponding carballylates.

Some Reactions of the Isomeric Amido-Benzic Acids.—Oechsner de Koninck. — Potassium, sodium, magnesium, and zinc, if heated in the absence of air with amido-benzoic acids, produce variable quantities of ammonia. If the same acids are heated with potassa, soda, baryta, strontia, magnesia, anhydrous or hydrated, zinc oxide, &c., we also observe the liberation of various proportions of ammonia. The various metals, oxides, and hydrates just mentioned do not develop the same colouring-matters with the three amido-benzoic acids.

Calculation of the Boiling-Temperatures of the Derivatives of the Paraffins by Terminal Substitution.—G. Hinrichs.—This paper requires the accompanying complicated diagram.

The Pyrogenic Carbides Formed in the Manufacture of Compressed Gases.—A. Brochet.—Among the numerous ethylenic carbides which may originate, the author has been able to identify six.

The Specific Gravity of Silks.—Leo Vignon.—In reply to M. de Chardonnet the writer maintains that the figures given by the latter are applicable not to silks in their original state but to specimens more or less "charged with metallic compounds."

Glycolysis in Blood.—Maurice Arthus.—Glycolysis in blood is a phenomenon of chemical fermentation. The ferment does not pre-exist in the blood, but is formed outside the organism at the expense of the white corpuscles, and seems to be in relation with the extravascular life of these elements. Glycolysis may be effected in the absence of elements actually living. It is effected exclusively outside the circulatory system like coagulation, with which it presents important analogies.

Bulletin de la Société Chimique de Paris.
Series 4, Vol. vi., No. 70.

Report made by M. Jungfleisch on behalf of the Committee of Chemical Arts upon the Frigorific Appliances Installed at the Morgue.—The Morgue having become an annoyance and possibly a danger to a very densely populated locality, it has been resolved to employ refrigeration. It was required that the bodies on their arrival at the Morgue should be exposed to a temperature of -15° to -20° . They were then to be placed in a hall in which the temperature should range from -4° to -1° , and which should admit of ten bodies being preserved at a temperature of -4° . The system of refrigeration employed is that of F. Carré, the agent in which is liquid ammonia. The apparatus acts by physical and not by mechanical means, as on account of the situation everything calculated to occasion oscillation had to be avoided. The hall in hot weather requires an hourly supply of 13,000 "frigories."

On Lighting Gas.—Prof. Vivian B. Lewes.—From the *Journal of the Society of Arts*.

No. 71.

This issue contains no chemical papers.

MISCELLANEOUS.

The Chemical Laboratory of Wiesbaden.—In the winter term, 1891-1892, there were fifty-four students on the books. Of these thirty-nine were from Germany, three from Russia, three from North America, one from Luxemburg, one from Switzerland, one from France, one from Holland, one from Belgium, one from Spain, one from Sweden, one from Batavia, and one from the Cape of Good Hope. Besides the director, Geh. Hofrath

Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and architect J. Brahm. The assistants in the instruction laboratory were three in number, in the private laboratory twelve, and in the Versuchsstation three. The next summer term begins the 25th of April. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Medical, 8.30.

Society of Arts, 8. (Cantor Lectures). "Mine Surveying," by Bennett H. Brough, Assoc. R.S.M.
Society of Chemical Industry, 8. "On Specific Gravities for Practical Purposes," by Dr. C. R. A. Wright, F.R.S. "On Artificial Musk," by Adolphe Baur, Ph.D. "Note on Rosin Oil," by F. H. Leeds, F.I.C., F.C.S.

TUESDAY, 5th.—Royal Institution, 3. "The Brain," by Prof. Victor Horsley, F.R.S.

Institute of Civil Engineers, 8.
Pathological, 8.30.
Society of Arts, 8. "The Red and White Races in Manitoba and the North-West," by the Rev. John McLean, D.D.

WEDNESDAY, 6th.—Society of Arts, 8. "The Future Trade Relations of Great Britain and the United States," by Robert McCormick.
Geological, 8.

THURSDAY, 7th.—Royal Institution, 3. "Epidemic Waves," by B.

Arthur Whitelegge, M.D., B.Sc.
Institute of Electrical Engineers, 8.
Society of Arts, 4.30. "The Agricultural Needs of India," by Dr. J. Augustus Voelcker.
Chemical, 8. "Platinous Chloride and its Use as a Source of Chlorine," by W. A. Shenstone and C. R. Beck. "The Action of Silicon Tetrachloride on Substituted Phenylamines," by Prof. Emerson Reynolds.

FRIDAY, 8th.—Royal Institution, 9. "Electric Meters, Motors, and Money Matters," by Prof. W. E. Ayrton, F.R.S.

Astronomical, 8.
Physical, 5. "Note on a Law of Colour in its relation to Chemical Constitution," by William Akroyd. "On the Construction of a Colour Map," by Walter Bailey, M.A. "A Mnemonic Table in connexion with Electrical Units," by William Gleed, M.A.

SATURDAY, 9th.—Royal Institution, 3. "Dramatic Music, from Shakespeare to Dryden," by Prof. J. F. Bridge, Mus. Doc.

ERRATA.—P. 147, col. 2, line 16, for "CrO₃" read "CrO₂". Line 42, for "CrO₃" read "Cr₂O₃".

CHEMICAL LABORATORY, WIESBADEN, GERMANY.

Director—Prof. R. FRESENIUS, Ph.D.

Practical Instruction in the Laboratory
Prof. R. FRESENIUS, Ph.D.
Prof. H. FRESENIUS, Ph.D.
W. FRESENIUS, Ph.D.
E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
Experimental Physics W. FRESENIUS, Ph.D.
Stoichiometry E. HINTZ, Ph.D.
Organic Chemistry Prof. E. BORGMANN, Ph.D.
Chemical Technology
Microscopy, with exercises in Microscopic work
Chemistry and Analysis of Foods
Hygiene
Practical exercises in Bacteriology
Technical Drawing, with exercises J. BRAHM.

The next Session commences on the 25th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL's Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

THE CHEMICAL NEWS.

VOL. LXV., No. 1689.

RELATION OF VOLTAIC ELECTROMOTIVE FORCE TO MOLECULAR VELOCITY.

By G. GORE, F.R.S.

IN a recent research published in the *Proc. Birm. Phil. Soc.*, vol. viii., p. 63, 1892, it is shown by means of an extensive series of sixty-four tables of measurements of mean volta-electromotive force, that the dilution of the liquid of a voltaic cell by means of water or alcohol, the liquefaction of either the positive or negative metal of the cell by means of mercury, the dilution of either of these amalgams by means of mercury, or the dilution of one solid metal by means of another in an alloy, is universally attended by an increase of mean electromotive force of the diluted and diluting substances, and consequently also of the actual electromotive force of the diluted one, provided that in all cases no chemical union or other chemical change occurs in the mixture. The manifest explanation of this extensive general result is, that by the act of solution or dilution, the molecules of the active substance are separated farther apart, and consequently acquire increased velocity of motion. In proportion, however, as chemical union occurs, the gain of electromotive force diminishes and is converted into a loss, and the loss is larger in proportion as the chemical union is stronger. The method enables chemical compounds in alloys, amalgams, and electrolytes to be distinguished from mere mechanical mixtures.

THE ACTION OF ALKALINE MERCURIC CYANIDE ON MALTOSE, DEXTROSE, AND DEXTRIN.

By J. ARTHUR WILSON.

COMMERCIAL glucose or starch sugar, as is well known, consists of varying proportions of dextro-glucose, maltose, and dextrin, together with more or less unfermentable matters. It is also well known that the accurate determination, nay even the approximate determination, of each of these carbohydrates is very difficult indeed; but for most purposes this is not necessary, the determination of the specific rotatory power and reducing power being all that is necessary, giving, as it does, an insight into the composition of the sample. In Allen's "Commercial Organic Analysis" (vol. i., p. 303), it is stated that alkaline mercuric cyanide has been applied by H. W. Wiley to the analysis of commercial starch glucose. This reagent is said to destroy the optical activity of dextro-glucose and maltose, whilst leaving that of dextrin unchanged. Further on in the work above mentioned (p. 304), it is said that "On the other hand, it has not been proved that boiling with alkaline mercuric cyanide wholly destroys the optical activity of maltose and dextrose, whilst leaving that of dextrin unchanged."

I have long since felt the want of an accurate process for the above purpose in the control of a well known industrial process, so that it was with feelings of pleasure that I turned my attention to investigate the truth or otherwise of the above statement. My experiments do not pretend to be at all exhaustive, but I think they prove that the method is of very little use for the determination of the proportions of a mixture of dextrose, maltose, and dextrin.

Solutions were prepared of maltose, dextrose, and dextrin, containing 10 grms. per 100 c.c. of pure substance. The purity of these sugars was proved by determination of the cupric oxide reducing power and also of the specific rotatory power.

The method of proceeding was as follows:—The optical activity of the solution was first determined. 10 c.c. of the sugar solution (= 1 gm. dry sugar) was boiled two minutes with a slight excess of solution of alkaline mercuric cyanide, made by dissolving 12 grms. pure mercuric cyanide and an equal weight of pure caustic soda in 100 c.c. of water. The solution was then cooled, acidified by HCl, and diluted to 50 c.c. After clarification by pure animal charcoal the solution was polarised in a 200 m.m. tube.

The results were as follows:—

Maltose.

Solution 10 grms. per 100 c.c.
Polarisation 200 m.m., (A) α +26°0.
Polarisation after boiling with alkaline cyanide, 200 m.m. (A) α +18°.
Polarisation on original concentration, +9°0.
Polarisation destroyed, +17°0.

No. 2.—Second experiment, but boiling four minutes, gave the same results.

Dextrose.

Solution 10 grms. per 100 c.c.
Polarisation 200 m.m., (A) α +10°85.
10 c.c. = 1 gm. boiled two minutes with slight excess of alkaline cyanide, cool, acidify, and dilute to 50 c.c.
Polarisation 200 m.m., (A) α +0°00.

Dextrin.

Solution 10 grms. per 100 c.c.
Polarisation 200 m.m., (A) α +37°2.
Polarisation after boiling two minutes with alkaline cyanide, (A) α 200 m.m. +6°7.
Polarisation on original concentration, (A) α +33°5.

Loss, +3°7.

The results of the above experiments show that the method of Wiley is of very little use for the examination of commercial starch glucose. I should like to mention that the dextrin used in the above experiments was not quite pure, but not sufficiently impure to account for the loss given above. The fact that the optical activity of dextrose is completely destroyed in the above reaction might make the method of some use for mixtures of dextrose and other sugars.

Tottington, March 29, 1892.

ON THE COPPER AND SILVER COMPOUNDS OF ACETYLENE.

At the last meeting of the Chemical Section of the Franklin Institute, Dr. E. H. Keiser gave an account of an investigation upon the composition of the explosive copper and silver compounds of acetylene. The paper will be published at length subsequently. The results obtained are in brief as follows:—When pure acetylene is conducted into an ammoniacal solution of silver nitrate, the yellowish white precipitate which is formed has, when dried, the composition represented by the formula C_2Ag_2 . It may in fact be regarded as acetylene in which both hydrogen atoms have been replaced by silver. The formula that has generally been adopted for this substance is $C_2H_2Ag_2O$. But such a compound contains only 83·71 per cent of silver, whereas in three specimens of the substance prepared by Dr. Keiser the quantity of

silver found was 89.32, 89.44, and 89.60 per cent. The formula C_2Ag_2 requires 89.9 per cent silver. That the compound contains no hydrogen was shown by exploding a weighed quantity of it in a glass tube which had been exhausted with an air-pump; no hydrogen was obtained.

A study of the compound formed by acetylene in ammoniacal cuprous chloride showed that it was similar in composition to the silver compound, although in this case it was much more difficult to obtain the substance perfectly free from water. Analyses showed that the composition of the substance after it had been dried in a vacuum over sulphuric acid agreed very closely with what would be required by the formula $C_2Cu_2 \cdot \frac{1}{2}H_2O$. The investigation will be continued.

REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg.

(Continued from p. 159).

III.—Melting of Steel.

IN starting a new branch of manufacture of special steel out of new materials, we prefer the use of coke crucible furnaces. The latter are cheap in construction, and the best thing is that while using them for experimental purposes they may be lighted or stopped any moment, with no inconvenience. That is not the case with the Siemens gas crucible furnace.

After many difficulties, we started the manufacture of tool steel for the market. The price was ten paper roubles per pood.

The gas furnace made on the average 4 to 4½ heats per twenty-four hours. The steel was ordinarily cast into 1½ and 2 pood ingots, 4 inches square; moulds being used. The ingots, after careful cleaning by chisels, were forged. The resulting bars, after inspection, were finished under a 1½ cwt. quick-motion steam hammer.

We made for the market three grades of tool steel: No. 12, for planing tools; No. 10, for drilling tools, chisels, and wood-working implements; No. 8, for cutting and stamping tools. These three grades contained in succession, on the average, 1.20, 1.00, and 0.85 per cent of carbon. The percentage of the other elements was as follows:—

	Per cent.
Manganese	0.18
Silicon	0.20
Sulphur	0.02
Phosphorus	0.03

In melting for tool steel, we used a mixture of puddled steel, old crucible steel, and Swedish cast-iron, or a mixture of Swedish iron and Swedish cast-iron. Each crucible charge (62 pounds) contained two-thirds of a pound of ferro-manganese. Very hard tools, specially ordered, were made out of steel prepared by melting a mixture of blister steel, Swedish cast-iron, and a small quantity of silicon spiegel (⅔ of a pound) containing 10 per cent of silicon and 14 per cent of manganese. This compound has a quieting effect on the blister steel, which melted alone and cast into moulds very often gives rising ingots.

We prepared pattern casting for many purposes, especially for some parts of the torpedo boats built at the Poutiloff Works. The crucible charges contained a mixture of puddled steel, basic steel, Swedish cast-iron, and about ⅓ of a pound of ferro-manganese. Each heat took about five and sometimes six hours. The additions to the steel before pouring it into the pattern moulds consisted of nearly 1.25 per cent of the above-mentioned silicon spiegel. When casting small articles, we used ferro-aluminium, but always in company with silicon pig-

iron (for a charge of 62 pounds, 0.6 of a pound of the former and latter alloys).

We desire to say a few words concerning the preparation of ferro-aluminium. As already mentioned, we used American aluminium, coming from the Pittsburgh Reduction Company (CHEM. NEWS, vol. lxx., p. 133). The best way to prepare the ferro-aluminium is as follows:—

Equal numbers of empty and charged crucibles were placed in the Siemens furnace. The charge consisted of 70 per cent of good grey pig-iron and 30 per cent of silicon pig-iron (10 per cent of silicon).

When the charges are melted, every time two crucibles are drawn out—one charged and one empty. Into the latter, 12 per cent of aluminium is added and the melted charge is quickly poured on to it; the mass is well stirred by means of an iron rod and re-poured again into the emptied crucible. Finally, the aluminium melts and the alloy is ready.

Having made many experiments, we advise not to use aluminium in the metallic state; it must be used in the alloy form.

Taking into consideration cheapness and good effect produced, we prefer the use of a reasonable quantity of silicon spiegel as addition in making steel for solid pattern castings, which are to contain for this purpose about 0.25 per cent of silicon.

ON THE DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILISERS CONTAINING COTTON-SEED MEAL.*

By F. B. DANCY, A.B.

(Concluded from p. 163).

It is believed that the disparity in all these cases is probably not so great as it should be; that is to say, that the incineration method as here used probably does not give the full content of phosphoric acid for this reason. The inferiority of the solvent power of nitric acid for phosphates to that of hydrochloric acid is well recognised. I believe that this inferiority is greater when the phosphate has been ignited. To test this an acid phosphate was chosen, of which 2 grms. were dissolved in nitric acid and hydrochloric acid, and the total phosphoric acid found to be 14.56 per cent. Another 2 grms. were then ignited for about the same length of time that it requires to incinerate 2 grms. of a cotton-seed meal fertiliser to complete ash and then dissolved in nitric acid. The determinations were parallel, so that each received the same amount of heating with acid, which was protracted. In the case of the ignited phosphate, undissolved portions were plainly manifest to the eye, and the percentage found was only 13.62. The undissolved portions were filtered out and readily yielded to hydrochloric acid, giving fulsome precipitate of phosphoric acid. Next, another 2 grms. were ignited and dissolved in hydrochloric acid, when the full content of phosphoric acid was readily yielded. Hence it is concluded that had hydrochloric acid been used to dissolve the six incinerated fertilisers employed in the above experiments, higher percentages would in all probability have been found. Fusion would have furnished an absolutely certain means of arriving at the undoubted maximum content of phosphoric acid, but time was limited, and simple incineration was resorted to on account of expedition; and solution in nitric acid instead of hydrochloric acid was employed after incineration, because, as the results were to be compared, it was advisable to employ the same solvent power in each case.

In addition to the six experiments described above,

* From the *Proceedings of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.*

attention is called to the following:—Two samples of cotton-seed fertilisers were procured in which another chemist had made determinations of total phosphoric by the nitric acid method. His totals were 9.13 and 9.33. I found by incineration and solution in hydrochloric acid 9.85 and 10.13, a difference of 0.72 per cent and 0.80 per cent respectively. Taking his own determinations of insoluble, the available by his analysis was 0.72 per cent short in the first instance (7.40 per cent when it should have been 8.12 per cent), and 0.80 per cent short in the second instance (7.50 when it should have been 8.30 per cent). The disparity here is excessive, but the fault is not due to the chemist, but to the method. Being one of the alternate methods of the Association of Official Agricultural Chemists, he had no reason to doubt its adequacy.

Having looked at one side of the determination of available phosphoric acid in fertilisers containing cotton-seed meal, let us turn to the other, namely, the determination of insoluble. As almost the entire content of phosphoric acid in the meal has been shown to be available, it might be anticipated that there would not be likely to be much difference in the determination of insoluble, whether the citrate-extracted residue is first incinerated or dissolved directly in acid. Such was found by experimentation to be the fact. In fact, in every case but one (and this was the same fertiliser that was the exception to the total rule, namely, the old one brought from the previous season) a slightly higher insoluble was found by dissolving in acid directly than after incineration.

The details of the two methods of determining the insoluble were these: After filtering from the citrate and thoroughly washing, the filter and contents were in the first instance incinerated and the ash dissolved in nitric acid (designated in the table below as "incineration"), and in the second instance the filter and contents were introduced directly into flasks and completely dissolved with nitric acid and a little hydrochloric acid (the "acid solution" of the table below). The samples used were the same as those used in the total experiments, with the exception of 110, which was not used.

		Insoluble phosphoric acid.				
		56.	76.	77.	78.	57.
Incineration	..	0.84	1.80	0.86	0.87	1.59
Acid solution	..	1.00	1.91	1.28	1.05	1.42
Difference	..	0.16	0.11	0.42	0.18	—

Whether the excess of insoluble by direct acid solution was due to mechanical loss in the incineration by the other method (which in these instances is not at all apprehended, though it is believed that care is necessary to, with certainty, guard against such loss), or whether, as is much more likely, it was due to imperfect solution of the ignited phosphate by nitric acid (a danger already pointed out), is not positively shown. But it should be remarked that in the case of 77, which is the case of greatest disparity, the undissolved portions were manifest to the eye, and it is the writer's conviction that had hydrochloric acid been used instead of nitric, there would have been no material difference in the results of the two methods, either in these particular determinations or in any other determinations. It is regarded as certain, therefore, that there will be found no material difference in the insoluble by whichever way determined.* This being true, the available will vary directly and exactly as the total; and, therefore, by just so much as a total is short on account of the inadequacy of the nitric

acid method when used on cotton-seed meal fertilisers, by just so much will the available be short.

Now a few words as to what method is adequate, and a very few experimental determinations on this point, and the subject will for the present be laid aside. It is a matter of regret to the writer that the time was not at his disposal for more extended experimentation on the subject. Nevertheless he is none the less convinced, on account of the limited number of experiments here presented, of the truth of the point urged.

In order to compare the total as made by several different methods, sample 110 was chosen. This sample was sent by a fertiliser company, who took a fair sample of a large lot of goods at their factory, thoroughly mixed the sample, and sent one-half to the writer and one-half to a chemist in another State. The total was determined first by fusing 2 grms. of the fertiliser with a mixture of equal parts of carbonate of soda and nitrate of potash, as giving with certainty the maximum content and furnishing a standard for comparison. It was then determined by incineration and solution in hydrochloric acid, by incineration and solution in nitric acid, by solution direct in hydrochloric acid with chlorate of potash, and lastly by solution direct in nitric acid and a little hydrochloric acid. Following are the results:—

	Per cent.
Fusion	10.14
Incineration and solution in HCl ..	10.09
HNO ₃ ..	10.07
Solution direct in HCl+KClO ₃ ..	10.11
HNO ₃ +little HCl	9.56

From the above it seems that in this case all the methods save the nitric acid methods were adequate, but it is not apprehended that this will hold good in all cases; for, while here incineration and solution in nitric acid sufficed, there is certainly the danger of imperfect solution already referred to; and while here also solution in hydrochloric acid with potassium chlorate sufficed, it has already been shown that this method failed to extract from the meal alone more than half its content of phosphoric acid.* Fusion is, of course, always adequate, but too time-consuming, if any other adequate method less so is at hand. It seems probable that incineration and solution in hydrochloric acid furnishes all that could be desired.†

It is in point to add that in this case the writer reported to the manufacturers a total of 10.11 per cent, this being an average of the first four determinations. The insoluble found by incineration and solution in hydrochloric acid was 1.47, making an available of 8.64. It is not known what method the chemist used to whom the other half of this sample was sent, but his total was 9.72, his insoluble 1.50, and his available therefore 8.22. Note that the two insolubles are practically the same, and that, therefore, his available is less than the writer's by practically the same amount that the writer's total is greater than his.

The following results, obtained on sample No. 3 (containing cotton-seed meal) of the samples sent out by Dr. Burney, the reporter on phosphoric acid for 1890, were submitted to that reporter, and are here appended as corroborative of the conclusions reached in the foregoing paper:—

	Per cent.
I. Total P ₂ O ₅ , by evaporation with Mg(NO ₃) ₂ , ignition and solution in HNO ₃	12.10
II. Total P ₂ O ₅ , by simple incineration and solution in HCl	12.08

* It did not suffice in sample No. 3 sent out by the reporter on phosphoric acid.

† Corroborated by determinations in sample No. 3 sent out by the reporter on phosphoric acid, which showed:—

	Per cent
Total P ₂ O ₅ by ignition with Mg(NO ₃) ₂ and solution in HNO ₃	12.10
Total P ₂ O ₅ by simple ignition and solution in HCl	12.08

* Corroborated by determination on phosphoric acid, reporter's sample No. 3, which showed:—

	Per cent.
Per cent insoluble P ₂ O ₅ by ignition and solution in HCl ..	2.67
Per cent insoluble P ₂ O ₅ by dissolving filter and all in HCl and a little HCl (without igniting)	2.64

	Per cent.
III. Total P_2O_5 , by solution in $HCl + KClO_3$, two determinations (11'78 and 11'74) averaged	11'76
IV. Total P_2O_5 , by solution in HNO_3 + little HCl , two determinations (11'49 and 11'56) averaged	11'53
I. Insoluble P_2O_5 . After filtering from citrate solution and thoroughly washing, the fil- ter and contents were ignited and dis- solved in HCl	2'67
II. Insoluble P_2O_5 . After filtering from citrate solution and thoroughly washing, the fil- ter and contents were put direct into a flask and dissolved in HNO_3 + little HCl	2'64

AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SECTION B.—CHEMISTRY AND MINERALOGY.

ADDRESS BY THE PRESIDENT,

WILLIAM M. HAMLET, F.I.C., F.C.S.,
Government Analyst, N.S.W.

WHEN I became aware of the honour conferred upon me in being elected to the presidency of this Section, the question arose in my mind as to what the scope and character of the time-honoured Presidential Address ought to be. Should we bring before us the old platitudes and mystic half-truths embodied in the obsolete theories of the past, or, on the contrary, should we not try to obtain a clear presentment of recent advances in the science? and to recognise, in fact, the real benefits conferred upon the race by our increased knowledge: to recognise that the advance onward is always towards raising and bettering the lives of those around us, to finally become the heritage of those who follow us in the chain of life. Nor is it the only function of a President to convey to his hearers the *résumé* of the year's work; this may be better done by the numerous and increasingly bulky year books. Who amongst us does not remember the revered name of many a President of the older Association in Britain who presented the everyday facts of our science in such a clear and attractive manner that we thought no more of the toil and the unyielding patience required in our work, but only of the high aims and possibilities, of the ultimate unity and full relationship of all natural knowledge. This sense sublime—

"Of something far more deeply interfused,
Whose dwelling is the light of setting suns,
And the round ocean and the living air,
And the blue sky, and in the mind of man:
A motion and a spirit that impels
All thinking things, all objects of all thought,
And rolls through all things"—

was in no small degree fostered by such annual addresses. How many of our past Presidents have there not been who seemed to act as the sign-post pointing to the Elysian fields of new researches,—who, by their help, counsel, and encouragement, inspired the earnest labourer in the pursuit of truth, and led him on to new discoveries?

The progress of Chemistry and Mineralogy in Australasia, upon which it is my privilege to address you to-day, is, from the nature of the circumstances, slow and beset with many hindrances. And this chiefly because the greater portion of our energies are devoted to the estimation of the monetary value of the natural and commercial products around us.

Here, in this later known part of our planet, we needs must spend a great deal of our time in work that can only advance science somewhat indirectly; so that it might be said that the record of the year with regard to original research work, were it given in its entirety, would read very much like Falstaff's hotel bill, showing

but a halfpennyworth of research to an intolerable deal of drudgery. This, I admit, must necessarily be the case with most of us in a new country, who if not engaged in teaching and organisation are compelled to spend our time in assaying minerals, or else in the pursuit of the agricultural, sanitary, or criminal investigations incidental to our rapidly growing centres of population. Chemists in Australia occupy places in the rear-guard of the advancing army of science; and while it may not be our fortune to be at the outposts skirmishing on the frontier of the knowable, yet we have daily recurring duties that are none the less necessary for the well-being of society; thus at least, we may presume to say that we indirectly help forward the general advancement of science.

Still, some work has been done during the year in spite of these drawbacks: and this includes the discovery of the alkaloids brucine and strychnine in the fruits of *Strychnos psilosperma*, by Professor Rennie and Mr. Goyder, of Adelaide, who find 0.32 per cent of the mixed alkaloids in some specimens sent them by Baron von Müller.

Additions to our knowledge of the Australian gums and barks have been made by Mr. J. H. Maiden, of Sydney; the first gum recorded from one of the Tiliaceæ, or Linden blooms—a metarabic gum obtained from *Echinocarpus* (*Sloanea*) *Australis*—has been examined, also the gum of the grass tree, and the resins in certain species of *Pittosporum* and *Araucaria*, while he finds the kinds of great aid in the diagnosis of the different eucalypts.

Conspicuous amongst Mr. Maiden's researches is his work on Wattle-barks,* which are found to contain from 15 to 46 per cent of tannic acid, and have already proved to be valuable for tanning purposes, and their cultivation found easily remunerative to the agriculturist.

Then may be mentioned Mr. Kirkland's discovery of gallium and indium in some specimens of blende from Peelwood, N.S.W., the details of which will form the subject of an interesting paper by Mr. Kirkland. The minute structure of several of our more important rocks and minerals is being carefully and thoroughly investigated by the Rev. J. Milne Curran, F.G.S., a gentleman who has lately been awarded the £25 prize and the medal of the Royal Society of New South Wales.

Not only is the presence of the rarer metals of interest, but it is satisfactory to note that some observers are making efforts to find out the actual state of combination in which elements occur. An instance of this has lately been mentioned to me by Mr. Atherton through Dr. Storer, who finds gold in the state of sulphide at Deep Creek, Nambucca, N.S.W. Quantities of the raw ore were treated with sodium sulphide, and the gold obtained as Au_2S_3 , there being only the merest trace left unacted on.

Much of this kind of work needs to be done in the Colony; and if such questions were investigated by men who understand what they are doing, it would go a long way towards facilitating the operations attempted in the smelting works, where carbonates, chlorides, oxides, and sulphides are often expected each to yield to the same kind of treatment.

Much has been said, and is still being said—though chiefly by speculators and mining share manipulators—about the vast mineral resources of Australia, and glowing accounts are set forth (in the prospectus be it observed) of reefs, leads, and auriferous deposits innumerable, where the precious metals are supposed to exist in most comfortable and payable quantities. But, when operations are well advanced, there comes the inevitable awakening, when plain facts clearly indicate that nature is not to be flattered with, notwithstanding the potency of a prospectus. Machinery rusting in idleness, useless furnaces, and other lumber remain as monuments of the unfortunate practice of erecting mining plant before the nature of the mine is

* "Wattles and Wattle-barks," by J. H. Maiden, F.L.S., F.C.S. Second Edition. Sydney: The Government Printer, 1891.

sufficiently understood. The dearly-bought lesson is this—that it is impossible for men who lack the necessary training in metallurgy to embark in adventures which, if attempted in other walks of life, would be considered madness. Yet the non-fulfilment of the expectations of those who invest in mining properties is ascribed to any cause but the right one.

The easy-going nugget-finding days are past, and have become a matter of history, while modern mining demands, more than ever, a larger share of skill, perseverance, and hard work. Smelting and reducing operations must necessarily become increasingly difficult as the richer ores become exhausted and new difficulties present themselves.

The problems of to-day are:—

1. Treatment of the so-called refractory ores.
2. Winning the precious metals from low-grade ores carrying but a few ounces to the ton.
3. The extraction of the metals from minerals holding some objectionable metal, or rather a metal that at present embarrasses the smelter—such, for instance, as the presence of zinc and sulphur in the Broken Hill ores.

To presume to deal with anything like a solution of these difficulties is quite beyond both my province and intention; but I would like to remind you of the sort of difficulty that blocks the way to success in many mines throughout Australia; and I, moreover, desire to point out some course of action that may probably be adopted in the near future (if I may make use of the expression), while social and labour difficulties stand like lions in the path whenever these problems are broached. However, come when it may, I foresee a time when other processes will supplant the expensive and crude methods hitherto attempted. Already there are companies and mine proprietors who perceive the want of processes better adapted to meet particular cases, and we hear a good deal about chlorination and wet methods for the separation of gold and silver.

The principle underlying all wet methods whatsoever is the chemical action of the electro-negative molecules, oxygen or chlorine, rightly and economically applied to suit the particular kind of ore to be treated.

Where sulphur is the *bête noir*, oxygen may be advantageously used if the metal be convertible into a soluble sulphate. Sulphur being absent, or easily removable by preliminary roasting, as in a great number of cases, then we may bring into operation the vigorous action of the little chlorine molecule—an instance of the phenomenon of that subject of solution which is profoundly interesting the minds of the chemists of the present day.

Now, as the source of the world's chlorine supply is the common salt we see on our dinner tables every day, this familiar and salutary article must become an object of absorbing interest. Strange as it may appear to many, it is hardly too much to say that the phenomenon presented to us of a spoonful of salt dissolving in a tumbler of water is under close observation, and forms the subject of investigation of the best chemical philosophers of our age.

It may also seem a strange and far-fetched idea, yet the attention now bestowed on the physical and chemical properties of the molecule in solution must eventually contribute to the perfecting of new methods of separating metals from other elements with which they are associated in the ore. Leaving the practical side of the subject for a time, let us see what is being done in this interesting domain of molecular mechanics,—let us track the chlorine molecule into space.

He who surveys the ever-widening boundary of modern chemistry cannot fail to be impressed with the increasing amount of attention bestowed on physical and general chemistry. It would seem as though a reaction had set in: instead of the appalling host of carbon derivatives, which no man can number, endless as they seem in their

protean permutations, we see a desire on all hands to know more of the varying phases of matter which were formerly passed by as trivial or commonplace; to picture the atom in space; to form clearer conceptions of the rushing together of atoms in the act of combination,—in a word to know something more definitely about chemical action. Thus am I led on to the subject of the molecule *per se*—the free ion—the whirling, eddying, ether-embedded molecule.

Our present position finds us in possession of the well-established—may I not say, the Impregnable—theory of an all-pervading ether describable as an elastic solid endowed with a great degree of rigidity. From the time of Young onwards this working hypothesis has commanded the assent of all thinking men, confirmed and strengthened as it is by the classic and firmly-founded work of Sir William Thomson, and others who have approached the subject from all sides.

Clearer perceptions also prevail with regard to the discontinuous or heterogeneous nature of matter, even of those solids which appear to our senses and to our most refined and delicate instruments as perfectly homogeneous; moreover, the kinetic theory, not only of gases, but of all states and conditions of matter, has received general recognition.

Yet another theory will, I am sure, commend itself to your earnest attention—one I have thought a good deal about for some years past, and which has been touched upon by Mendeleeff eighteen months ago when lecturing at the Royal Institution in England.

The idea may be considered a wild speculation by some; but I am bound to believe, judging by analogy with the magnificent conceptions presented to us by modern astronomy, and by the observed behaviour of matter as shown lately by the work and discoveries of Crookes, Thomsen, Ostwald, Arrhenius, Van't Hoff, and many others, that, just as the systems of worlds, suns, stars, and planets roll in limitless space, so rolls the atom, but at enormously increased velocities in symmetrical order like double stars, or in systems comparable to suns and their accompanying satellites—the complete self-existent undissociated molecule being comparable to a given solar system coursing through space.

The work of Maxwell, Faraday, Helmholtz, Lodge, Fitzgerald, Hertz, and Sir William Thomson, men, who, like Huxley's ideal possessor of a liberal education, can "spin the gossamers as well as forge the anchors of the mind," all contribute towards clearing up the mystery surrounding the thing daily handled and observed by the chemist—the familiar thing we call "matter."

Putting aside for the moment the idea as to whether the atoms are or are not portions of the ether differentiated off from the rest by reason of their vortex motion, we have in the omnipresent ether, at any rate, the space, the playground, for the atom, whose unseen but energetic movements we have learned to speak of as heat and chemical action.

Having, then, granted a place in the universe for the ubiquitous atom, the chemist must endeavour, however dimly it may be, to picture to his mind its relative position, its own proper motion, its translatory motion, and, above all, its influence upon the ether when rocked by the waves set up by vibrating masses of atoms at a distance. When this is known we shall be able perhaps to account for the specific differences presented to us by matter.

In its simplest aspect we may think of the substance of the universe, at least of that which appeals to our senses, as consisting of what we arbitrarily call matter, and of its smallest portion as the invisible atom—an idea held by ancient philosophers some three centuries before Christ; the smallest quantity assumed to exist freely in space under known conditions being the molecule. From what we have seen and from all we know of infinitely minute particles of matter, can we think or conceive that these molecules are huddled together like a chaotic heap

of bricks? Assuredly not,—at least not in a definite compound; and the truth is borne in upon us at the thought of the microscopic yet symmetrical crystal. Looking about for a familiar and universally known substance, we have in water an instance of a symmetrical molecular system, whether under the form of solid ice, liquid water, or gaseous steam, made up of three atoms.

It will greatly assist us in our contemplation of the molecule if for the nonce we magnify these atoms several million times beyond their actual size. We should probably see a small sphere rotating about their own axis, and at a given distance two larger spheres also rotating about their own axes, but travelling in a definite orbit around the smaller sphere, the three together forming a system revolving in one plane with its own individual precision, the whole system capable of moving at a great velocity in any possible direction.

Calling these individual planets in the molecule by their received names, we see oxygen as a central sun with two large primary planets both called hydrogen, situate at equal angular distances from each other, but with nothing known at present to distinguish either of the hydrogen planets from each other.

Suppose, now, their orbital velocity be caused to diminish by friction and to finally cease, we should have each hydrogen planet distant 180° from one another. Placing three such systems with no orbital motion over each other so that the hydrogen satellites shall be equidistant, a straight line passing through and intersecting each of the centres of the oxygen spheres will form a hexagon.

Now, it is a fact that water in crystallising to snow and ice assumes the form of the hexagon. May not this cessation of the orbital motion determine the act of crystallisation, and, on the other hand, the widening and opening out of the orbit determine the expansion, while the friction of hydrogen against hydrogen satellite determines the heat caused by compression?

In trying to realise these things I have asked you to magnify the dimensions of the atom in the structure of matter; this has already been done, as you well know, by Sir William Thomson; but, as a better estimate of the size of the atom will be gained, his calculation will, I think, bear repetition. "Imagine," he says, "a globe of water or glass, as large as a football (or, say a globe of 16 c.m. diameter), to be magnified up to the size of the earth, each constituent molecule being magnified in the same proportion. The magnified structure would be more coarse-grained than a heap of small shot, but probably less coarse-grained than a heap of footballs."

A glassful of pure water, then, consists of an enormous and unthinkable number of molecules, each consisting of a complete system of atoms arranged by law in a definite and determinate order, like the orbs we see

"In the sacred glory of the azure night."

It follows that in this mass of water there must be intra-molecular spaces, and that the molecules are everywhere throughout the liquid jostling, colliding, and sliding over one another. It also follows that, if we can communicate motion from without, the mere gliding of molecule over molecule will give way to sharp collision, impact succeeding impact, until the crowd of molecules is in a state of great internal commotion. Such an effect is brought about by the mere application of heat, and the energy of this motion is capable of being accurately measured.

This internal bombardment of molecules may proceed further, until cohesion and surface tension is overcome and the gaseous state is arrived at.

Regarding matter as being thus constituted, what should happen when we throw a few grains of salt into water? Clearly, it must be that as soon as the molecules of sodium chloride come within range of the water molecules friction and collisions ensue, the nearest salt molecules being driven into intra-molecular space. The amount of heat necessary to undo the crystalline struc-

ture—in other words, the motion acquired by the sodium chloride on coming into solution is abstracted from the water molecules; that is to say, work is done by the water molecules, hence a reduction of temperature in the liquid. Had we substituted potassium iodide with its greater molecular weight instead of the sodium chloride, the reduction of temperature would be greater. The solution of a salt in water may be regarded as the removal of molecule after molecule in the crystalline architecture, the whole mass finally reaching one uniform state of motion—*i.e.*, equilibrium of temperature and action. The molecules thus dislodged from their recent crystalline structure are free to spin through the liquid as double stars, having a diminished degree of attraction for each other owing to their approximately similar atomic weight. Thus it comes to pass that we have a stage of incipient dissociation, a large proportion of the atoms being liberated in the free state or dissociated into their ions,—a conclusion arrived at by Arrhenius in 1887, and quite independently by Planck in the same year.

The apparent decomposition of a salt solution, *i.e.*, an electrolyte into free ions, is considered by some to be a process of direction and not one of real decomposition; but I think myself that it is one of oscillation between mere direction on the passage of the current on the one hand and dissociation on the other.

In the present controversy between association and dissociation there is reason to believe the advocates of both systems to be right so far as the facts are concerned, the phenomena presented by the hydration of sulphuric acid not being on all fours with the facts brought to light in cases of salt solution. However, the day will soon dawn when the whole subject relating to chemical energy will be fully elucidated, and means found for its precise measurement. It is now a veritable mine of intellectual activity, and it is no wonder that new facts are constantly being recorded.

We may expect that, with such an array of facts such as are now given to the world by Ostwald, Van 't Hoff, Gladstone, Pickering, Arrhenius, Armstrong, and others—facts that slip easily into their proper places in the great fabric of Physical Science—that some master mind must sooner or later arise who shall so co-ordinate, interpret, and arrange them as to deduce therefrom the laws of chemical energy and affinity. Mendeleeff, in recognising this, bids us anticipate such a grand realisation. He says,* "the invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for astronomy and mechanics in the days of Newton." It is well to remember that Newton devoted much time to chemical experiments, and while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics.

As the avowed object of most of the addresses that are inflicted upon us should be "to point a moral: to adorn a tale," we ask ourselves, Is there no interest in this question of salt-solution for us here in Australia? I venture to believe there is. And thus we come back to the question of the action of solvents generally, and the practical application of them in what are called wet processes in mining and metallurgy.

The extraction of metals from their ores has been effected from time immemorial by the well-known methods

* "An Attempt to Apply to Chemistry one of the Principles of Newton's Natural Philosophy": a Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

of smelting, the object generally aimed at being the separation of the metal in the molten state by the addition to the ore of some mineral or earthy substance to cause the mixture to fuse, flow, or flux while subjected to the great heat of a furnace, the metal separating out by itself in a more or less pure condition.

The cost of such a scheme of well-planned operations as these will, of course, vary with the degree of richness of the ores, the cost increasing with the poverty of the ore treated, a limit soon being reached which depends on local and other conditions, and the poor ores can only be regarded as so much useless rubbish that will not pay for smelting. In such cases a wet process for extracting the metals might be advantageously employed, and we may dissolve the precious metals in a watery solution and collect them by suitable means. To the miner who is unfamiliar with such a process it sounds an impossible and an uncanny way of doing things. However, several wet methods commend themselves to the metallurgist in cases where the ores are too poor to be worked economically by any other means.

Speaking generally, the end in view is to obtain the metals in a soluble form, either as chloride, sulphate, or cyanide, and then to remove them from the liquid by precipitation. In this way we can separate out gold, copper, zinc, silver, and lead.

In the case of chlorination the sources of the active chlorine are:—

1. The decomposition of bleaching-powder either by acids or acid sodium sulphate.
2. The direct use of the chlorine liberated by electrolysis.
3. Roasting the ore with salt.

The first of these methods is open to serious objection owing to the wasteful loss of chlorine, and the difficulty of transporting oil of vitriol over rough country. Both of the other methods have much to recommend them in a country like Australia.

Amongst the simplest processes suitable for Australian ores—one adapted for the extraction of silver from ores not rich enough to pay for smelting, or from ores that do not easily yield to ordinary treatment—is the Joachimsthal process suggested by the late Dr. Percy and Von Paterna, also known as Kif's method.

Many modifications and improvements have been made on the original process, and the names of Henderson, Claudet, and others are associated with it, the modifications being made to suit the great variety of ores treated.

The ore, broken small, dried if necessary, and crushed fine under the stampers, is mixed, with or without preliminary roasting, according to the nature of the ore, with 12–15 per cent of common salt, and roasted six to ten hours. The active chlorine molecule seizes the copper, lead, gold, and silver molecules to form the chlorides of these metals. On now soaking out the cooled product in water—the operation termed leaching—a portion of the now soluble metals are removed, being dissolved in the salt water. Allowing the earthy impurities to separate, this liquid is drawn off and set aside for after treatment. The roasted ore is further lixiviated by means of a cold solution of 1–2 per cent sodium thiosulphate, and added to the first liquor. From this the lead is removed as “white lead” by soda ash, yielding at once an article of commercial value, and the copper and silver are both separated out by precipitation with sodium or calcium sulphide; the product, containing 25 per cent of silver, is dried and roasted, being then available as a marketable commodity. This process has been successfully carried out at Rivertree, N.S.W., by Mr. Hall, of Brisbane, who finds that 85 per cent of the silver present in low grade ores may be obtained in this way.

Another process lately brought into use in Queensland and in Victoria is the “Pollok Chlorination Process,” more especially adapted for gold ores. Chlorine under great pressure is employed to dissolve the metal, the gold

being separated by an iron salt. The details of this process is given by the late C. S. Wilkinson, who inspected its working while in Glasgow about a year ago (Report, Mines Department for 1899, p. 213. Sydney: Government Printer, 1891). Mr. Wilkinson also described the Macarthur-Forrest cyanide process, in which a weak solution of potassium cyanide is used to dissolve out the precious metal, which is then removed by metallic zinc. The process is being worked at Ravenswood, in Queensland.

The chief considerations that have to be taken into account in any of these methods of working must necessarily include the question of easy transport across country of the materials to be used, and the presence of an adequate water supply. The future of silver reduction in Australia must surely be an interesting one to all chemists and metallurgists; and when the labour question shall have been righteously adjusted between man and man, and the spread of technical education produces the skilled workman, there will be no reason why minerals carrying what are now considered ridiculously small quantities of gold and silver should not be economically worked.

A promising step in the right direction is the idea of producing chlorine on the spot from common salt by means of the current of electricity from an ordinary dynamo. The production of chlorine by electrolysis is already a *fait accompli*, and bids fair to prove successful as a commercial undertaking. A process has been patented by Messrs. Richardson and Holland, and recommends itself on the ground of its portability, the materials requisite for working the same being easily transported over great distances. The principle is based on the fact that common salt is decomposed and resolved into its ions, as we have seen, the chlorine being set free next the anode and sodium at the cathode. The chlorine is collected from the surface, while caustic soda remains in the liquor. The chlorine may, however, be allowed to reunite with the sodium, as hypochloride, if desired. A drawback to its use at first was the resistance caused by the insertion of porous partitions used to separate the ions. This greatly militated against its commercial application, as did the polarisation caused by the evolution of hydrogen from the decomposition of the water present. To overcome these difficulties, the porous partition of the decomposing tank is reduced in size, and copper oxide is introduced to enable the hydrogen to combine with its oxygen, thus leaving behind metallic copper, which is re-oxidised by heating in a current of air and used over and over again. The process may obviously be used in the manufacture of caustic soda and sodium hypochlorite as well as chlorine, according to requirement.

(To be continued.)

Synthetic Formation of Acetylene at the Expense of Bromoform.—P. Cazeneuve.—Bromoform, in contact either with silver-powder or with moist zinc-copper, constitutes an abundant source of acetylene.—*Bull. de la Soc. Chim. de Paris.*

Detection of Isocholesterine.—E. Schulze (*Zeit. fur Phys. Chemie*).—The author utilises the colour-reactions produced with acetic anhydride and sulphuric acid. If the ischolesterine is dissolved in acetic anhydride with the aid of heat, allowed to cool, and a drop of concentrated sulphuric acid is added, the solution takes first a yellow colour, which passes into an orange. The liquid displays also a green fluorescence. If ischolesterine is dissolved in chloroform and acetic anhydride, and sulphuric acid are added, the same phenomena occur. This reaction is very sensitive, and serves for the detection of 1 m.grm. ischolesterine. Cholesterine reacts also with the same reagents, but the colours obtained are quite different from those of ischolesterine.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 25, 1892.

Professor S. P. THOMPSON, Vice-President, in the Chair.

Miss L. E. WALTER was elected a member of the Society.

"A Note on the Electromotive Forces of Gold and Platinum Cells" was read by Prof. E. F. HERROUN.

Modern text-books put gold before platinum in Volta's electropositive series, and thus one is led to expect a greater evolution of heat when gold combines with, say, chlorine than when platinum does so. This, however, is not the case: for Julius Thomsen gives for the heat of formation of platonic chloride a value considerably greater than that for auric chloride. Gold should therefore be electronegative to platinum. The few experimenters who have tested such cells arrived at different conclusions; hence the author took up the subject, and examined experimentally the E.M.F.'s of zinc-platinum and zinc-gold cells, the metals being immersed in solutions of their chlorides of equal molecular strength. Instead of platonic chloride, a solution of sodio-platonic chloride was employed. From Thomsen's thermo-chemical data, the E.M.F. of such a zinc-platinum cell should be 1.548 volts; whilst experiment gave values between 1.70 and 1.473, according to the previous history of the cell. The average E.M.F. was about 1.525. Allowing the cell to send a current reduced the E.M.F. considerably, but it partly recovered on standing. Renewing the sodio-platonic chloride reproduced the high initial E.M.F. of 1.7 volts. This high value and the uncertainty of the E.M.F. after sending a current the author believed due to dissolved oxygen. Zinc-gold cells, the metals being immersed in solutions of their chlorides, gave more constant results, the maximum being 1.855 and the minimum 1.834 volts; whereas from thermo-chemical data the E.M.F. should be 2.044. On replacing a gold plate by a platinum one, the E.M.F. fell to 1.782.

Other experiments showed that gold is slightly electropositive to platinum in water or dilute HCl, but in aqua regia the positions are reversed.

Prof. AYRTON said the experimental E.M.F.'s were fairly close to the theoretical values, and thought the differences might arise from occlusion of gases, which, although not taken into account in the thermo-chemical experiments, might have considerable effect on the electrical values. Platinum especially had remarkable occluding properties.

Mr. ENRIGHT pointed out that if any gases were disengaged by the reactions in the cells, their thermal values must be allowed for.

The Chairman (Dr. THOMPSON) believed that some discrepancy between the calculated and observed values of the E.M.F.'s might be due to the calculations only being carried to the first degree of approximation. The complete expression contained, amongst others, a term depending on the temperature coefficient of the cell. On the subject of variation of the sign of E.M.F. with the strength of solutions, he said he had observed similar effects with cyanide solutions.

Dr. HERROUN, in reply, said care was taken to expel as much of the occluded gas as possible before using the plates, and no gases were formed in the reactions. To Dr. Thompson he pointed out that Clarke's cell had an E.M.F. greater than that calculated from thermo-chemical data; hence the temperature coefficient ought to be positive, but, as a matter of fact, it is negative. The discrepancy between the calculated E.M.F. and the observed he believed due to inaccurate determinations of the thermo-chemical constants of mercury salts.

A "New Instrument for Showing the Effects of Persistence of Vision" was exhibited and described by Mr. E. STUART BRUCE, M.A. The instrument, which the author calls an "aërial graphoscope," consists of a narrow wooden lath mounted on a whirling machine so as to be rotated rapidly in its own plane. The lath is tinted grey in the centre, and shades off to white at the ends. When rotated, it presents the appearance of a nearly uniform screen or disc, owing to persistence of impression. Ordinary lantern slides were projected on this aërial screen with remarkable effect, for the pictures appeared suspended in mid-air. The author explained that the object of darkening the lath near the middle was to give a more uniform illumination to the picture or disc. On covering up the centre portion of the lath with white paper, the middle of a picture projected on it was much more strongly illuminated than the edges.

Mr. BLAKESLEY pointed out that the effect produced by darkening the centre of the lath might be attained by painting white sectors on a black lath.

A Paper on "Some Electrical Instruments" was read by Mr. R. W. PAUL, and the apparatus exhibited. He first described a new form of standard ohm, the distinguishing feature of which is that the wire is wound in one flat spiral, and contained between two thin brass plates. The whole of the wire is thus practically at the same level in the water-bath, and therefore will be more likely to be at uniform temperature throughout than coils having considerable vertical depth. A thermometer passing down the central tube has its bulb on the same level as the wire, and another thermometer placed in the water-bath at the same level serves to check the uniformity of temperature. In order that the width of the coil may not prevent convection currents in the bath, the screws which fix the two brass plates together have large holes through them. Dr. Fleming's suggestion of forming the upper ebonite insulator into an oil cup has also been carried out.

A new form of Wheatstone bridge was next shown possessing all the advantages of the dial pattern, combined with great facilities for cleaning. There are four resistances in each proportional arm, and the adjustable arm has four sets of coils, units, tens, hundreds, and thousands, each set consisting of ten equal coils. The ends of each coil are connected to brass sockets fixed about an inch apart on the ebonite top. Successive coils are put in circuit by placing a plug attached to a flexible cord in the required socket.

Special contact bars are provided, whereby two or more coils of any set of ten may be put in parallel arc so as to get accurate resistances of large carrying capacity. These bars are also useful for obtaining high ratios between two resistances, a point of considerable importance in the testing of large resistances. Amongst the advantages claimed are—better insulation, avoidance of surface leakage by providing ample facilities for cleaning, small block error, which is constant and easily measured, and no loose plugs required. Each set of ten coils may be used as separate circuits. By means of two travelling terminals the box may also be used as a potentiometer reading to 1 part in 10,000.

A reflecting galvanometer with several improvements was then exhibited and described. The coil is supported on an ebonite pillar fixed to a tripod, below the centre of which controlling magnets on the Siemens principle are pivoted. The pillar gives good insulation from earth, and the adjustment of the control can be made without setting the needle in vibration. The two halves of the coil are wound according to Sir W. Thomson's law, and fixed in ebonite boxes turned to fit them. They are thus kept permanently in shape. The ebonite boxes are interchangeable, so that either high or low resistance coils can be used in the same stand. The coils have separate terminals, and can therefore be used in series or parallel, or differentially. The mirror is placed in a metal box

below the coil. When intended for an astatic instrument magnets are put behind the mirror, and the metal box serves to damp the vibrations. For ballistic work the mirror has no magnets on it, and the damping may be regulated by sliding in or out a plug which carries the window of the mirror box.

Mr. SWINBURNE inquired whether the plan of using two vertical magnets to form an astatic system had been tried, and with what result. He also asked if dial bridges made with switches instead of plugs would not be advantageous.

Dr. SUMPNER said vertical needles had been used at the Central Institution and found satisfactory.

Mr. A. P. TROTTER wished to know whether there was any very great advantage in designing galvanometers with a minimum amount of wire. A galvanometer was often required for many different purposes, and it did not follow that one with a minimum amount of wire was the best all-round instrument.

Mr. C. W. S. CRAWLEY made inquiries as to the magnitude of the block error in the form of Wheatstone bridge shown, for he thought the flexible cords would make it considerable. In reply to Mr. Swinburne he said he had found the variations in switch bridges greater than in plugs.

Prof. S. P. THOMPSON thought it was not generally known that the best shape of galvanometer coil depended on whether the instrument was to be used as an ammeter or voltmeter. The shape determined by Sir W. Thomson was a voltmeter coil; that for an ammeter was much shorter axially.

Mr. PAUL, in reply, said he used one or other shape of coil according to the use for which the galvanometer was intended. The block error in the Wheatstone bridge was very small and quite negligible for most purposes. When very great accuracy was required the error, being constant, was easily measured and allowed for.

NOTICES OF BOOKS.

Lessons in Elementary Chemistry, Inorganic and Organic.

By Sir HENRY E. ROSCOE, LL.D., F.R.S., late Professor of Chemistry in the Victoria University, Owen's College, Manchester. London: Macmillan and Co., 1892. Small 8vo., pp. 503.

THIS favourite manual has now reached its sixth edition, besides having been many times reprinted with slight corrections. The author in his introduction considers the decomposition of some of the supposed elements into simpler ingredients as possible, or even likely.

The lessons on the periodic law, on spectrum-analysis, and on solar and stellar chemistry, are exceedingly valuable; quite equal, in fact, to what we often find in larger and more pretentious books.

The distinction between an organic substance and an organism is here clearly explained, and may save many students from dreaming of the synthesis of grain, fruits, &c.

On p. 339 we find an error doubtless clerical or typographic in its origin. It is there stated that "aluminium and ferric acetates are used in large quantities by dyers and tissue printers under the commercial names of red and black liquor." Iron liquor is not a ferric but a ferrous acetate.

At the end of the book there follow a number of questions and exercises which the student is advised to answer and to work out. But they are not said to have been "set" by any Board or Department, and throughout the book we can find no reference to any examination. This work must take rank among the few elementary treatises on chemistry which have a definite and legitimate *raison d'être*.

Soils and Manures. By J. M. H. MUNRO, D.Sc., F.I.C., F.C.S., &c. With chapters on Drainage and Land Improvement by JOHN WRIGHTSON, M.R.A.C., F.C.S. London, Paris, and Melbourne: Cassell and Co. Ltd., 1892. Small 8vo., pp. 275.

THIS work is one of the agricultural text-books published by Cassell and Co. under the general title "The Downton Series." Although one of the authors of this little book announces himself as "Examiner in Agriculture under the Science and Art Department," we find here no trace of the examinational taint. There are no lists of questions which have been asked anywhere on any occasion, and of course no sets of replies. The authors write not with reference to any possible examination, but with the wholesome and honest purpose of enabling their readers to know, and this purpose is very well effected. It is pleasant to see in what clear and simple language the nature of soils and the properties of their ingredients are explained, in a manner which certainly pre-supposes no chemical training on the part of the reader.

Humus, or vegetable mould, after having been first regarded as the sheet-anchor of the farmer and gardener, and then decried as next to useless, finds here a fair appreciation intermediate between these extreme views. The reader finds here that humus contains mineral food, is a store of nitrogen, keeps soils open, supplies carbonic acid, retains water, and absorbs manures.

Certain pieces of traditional wisdom current among our farmers, and too often simply ridiculed, are shown here to have in them a portion of truth. Thus, the proverb,—as we might almost call it,—that lime "enriches the father but impoverishes the son," is a one-sided expression of the great truth that no soil ought to be continuously manured with one substance only.

As real plant-foods the author enumerates nitrogen, phosphorus, potash, lime, sulphur, magnesia, chlorine, with a little soluble silica and a trace of iron oxide.

It is here decidedly admitted that leguminous plants procure nitrogen—though not necessarily all their nitrogen—from the air. The directions given for experiments, whether in the field or in pots, will prove very useful. The condemnation of nitrate of soda, and indeed of all chemical manures, as exhausting the soil, is shown to be founded on a myth. Agriculturists, both in France and Germany, are now considering that the keeping of stock on purpose to supply manure may be dispensed with. This, indeed, seems to have been thoroughly proved by Ville.

The remarks on sewage manure, especially when applied by irrigation, are very sensible. The writer says: "Large crops of rye-grass, mangolds, rhubarb, onions, cabbages, celery, osiers, and other produce can be, and are, grown on these farms, but not, as a rule, profitably. No one would complain much of this if the sewage ceased to be a nuisance, which is not always the case. There it is, Sunday and weekday, winter as well as summer, when the ground is bare as well as when growing a crop. Even if frost-bound for weeks there is the liquid to be disposed of somehow, the manager or farmer being in the position of having a very weak manure (valued at from a penny to twopence per ton), forced on him all the year round, instead of only the few months when he really wants it, and in quantities generally far greater than the land at his disposal requires."

Such outspoken truthfulness will in certain quarters not be heard without horror. Dr. Munro will next be "speaking holy words," if not to the Lord Lysimachus to some Royal Commissioner!

Almost the only shortcoming which we meet in this work is in the section relating to the value of manures. It must be admitted that manures have two distinct values, a commercial and an agricultural. Either of these may fluctuate independently of the other. The market value is a mere question of supply and demand; the agricultural value turns upon alterations in quality. A good

nstance of this is found in Peruvian guano. Since it was first brought into use the available supplies have been much reduced, some of the best deposits having been quite exhausted. Hence its commercial value has been well maintained. At the same time its percentage of nitrogenous matter has fallen off, whilst that of sand and moisture has increased. Hence its agricultural value has been reduced. The farmer can be recommended to buy a manure only if its agricultural value is decidedly higher than its market price. This work may be warmly recommended.

The Climatologist. A Monthly Journal of Medicine devoted to the Relation of Climate, Mineral Springs, Diet, Preventive Medicine, Race, Occupation, Life-Insurance, and Sanitary Science to Disease. Vol. II. No. 1.

We do not see that in this journal there is anything which falls legitimately within the purview of the CHEMICAL NEWS.

CORRESPONDENCE.

PROPOSED STANDARD METHODS OF WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—The importance of having standard methods of water analysis (especially technical water analysis), agreed to by chemists, at least in the United Kingdom, seems to me never to have been so necessary as at the present time. Now that authorities are being forced to do something to purify their sewage and works, their waste liquors from manufacturing processes, difficulties will arise, no doubt, as to the methods to be used of deciding the purity, or otherwise, of the water in question. Methods of determining the most common impurities are by no means what they might be, and the use of inaccurate processes may give rise to unpleasantness between parties.

The subject is a large one, and a deal of work would have to be done before any scheme could be adopted; nevertheless, it seems to me that this ought not to prevent an attempt being made. I trust, therefore, that chemists will expound their views in the columns of the CHEMICAL NEWS, and it is perhaps, further, not too much to expect that something may be done towards the realisation of this desirable end.—I am, &c.,

J. ARTHUR WILSON.

Tottington, March 30, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 12, March 21, 1892.

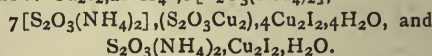
Study of the Properties of Amorphous Boron.—Henri Moissan.—This memoir will be inserted in full.

Preparation of Boron Iodide.—Henri Moissan.—A question of priority as between the author and M. Besson.

Origin of the Colouring-Matters of the Vine; on the Ampelochroic Acids, and on the Autumnal Colouration of Plants.—Arm. Gautier.—This paper will be inserted in full.

Determination of Chemical Equilibria in Dissolved Systems.—Georges Charpy.—This paper cannot be intelligibly reproduced without the accompanying diagram.

Combinations of Cuprous Iodide with Ammonium Hyposulphite.—E. Brun.—Three compounds may be obtained: $\text{Cu}_2\text{I}_2 \cdot 2\text{NH}_4\text{I} \cdot 8[\text{S}_2\text{O}_3(\text{NH}_4)_2]$,



The first of these bodies is soluble in water, but the two others are insoluble. All are gradually decomposed by heat. The potassium and sodium hyposulphites give analogous compounds, and other iodides, e.g., those of silver and lead, produce similar substances which the author proposes to study.

The Speed of Decomposition of the Diazo-Compounds.—J. Hausser and P. Th. Mueller.—A mathematical paper not susceptible of useful abstraction.

On Certain Bases, Homologues of Quinine.—E. Grimaux and A. Arnaud.—The authors have obtained and studied the propylic, isopropylic, and amylic derivatives of cupreine.

The Essential Oil of Licari kanali.—Ph. Barbier.—The author has experimented upon licareol, $\text{C}_{10}\text{H}_{18}\text{O}$,—a colourless liquid extracted from the oil of licari. Licareol is of an alcoholic nature, and must rank among the secondary alcohols.

Combination of the Fatty Acids with the Ethylenic Carbides.—MM. Béhal and Desprez.—The authors have succeeded in fixing the fatty acids upon the ethylenic carbides, obtaining caprylene and heptylene acetates and the diacetate and propylglycol.

Natural Synthesis of the Vegetable Hydrocarbons.—M. Maquenne.—Heptene must take rank among the inferior homologues of turpentine, $\text{C}_{10}\text{H}_{16}$, or even menthene, $\text{C}_{10}\text{H}_{18}$, which is formed in the action of phosphoric anhydride upon menthol.

The Presence in Straw of an Aërobic Ferment, Reducing Nitrates.—F. Bréal.—The author has observed a ferment in vegetable débris, which acts in an inverse manner to the nitric ferment of Schlessing and Müntz. He prepares diphenylamine sulphate for detecting nitrates in the following manner:—He boils pure sulphuric acid so as to expel any trace of nitric acid which may be present. In 100 grms. of the acid, when cold, he dissolves 1 grm. of diphenylamine, previously washed in distilled water and dried. He then adds 25 c.c. of distilled water.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 1.

Gasometric Alkalimetry, and on the Application of Potassium Ferricyanide in Gasometry.—Julius Quincke.—This bulky dissertation, which includes several pages of tables, does not admit of useful abridgment.

Acid Potassium Tartrate as Original Standard Substance for Acidimetry and Alkalimetry.—Prof. Dr. A. Bornträger.—Already inserted.

Volumetric Determination of Phenol.—Dr. R. Bader.—If to an aqueous solution of pure phenol mixed with a few drops of an alcoholic solution of symmetric trinitrobenzol we drop in slowly dilute soda-lye, the liquid remains colourless as long as free phenol is present, but the slightest excess of alkali is recognised by a distinct "onion-red" colour. The solution of trinitrobenzol required is prepared by shaking up repeatedly a knife-point full of pure, symmetric trinitrobenzol (melting-point 122°) with 50 c.c. of absolute alcohol and filtering. It must have only a very faint yellowish colour, and must be preserved in a dark place. For determining phenol in a watery solution he proceeds as follows:—He prepares colourless solution, not too dilute, containing, if possible, not less than 20 grms. per litre; of this 50 c.c. are poured

into a beaker, and there are added 2 to 3 drops (not more) of the trinitro-solution above mentioned. The liquid must remain perfectly clear and colourless. Hereupon normal soda-lye is allowed to fall in drop by drop, whilst the glass is constantly shaken. Towards the end of the reaction the liquid takes a scarcely perceptible yellowish tint. When this point is reached the titration is best continued in the following manner:—2 to 3 drops of soda-lye are added at once, the glass is shaken up, and this is repeated until the reddish-yellow colour produced by the soda no longer disappears. The last 3 drops must be deducted from the total quantity of the normal soda-lye consumed. The end of the reaction is best recognised if we place the beaker during the experiment upon a white porcelain plate. As regards the accuracy of the results they leave nothing to be desired if the solutions of phenol are sufficiently concentrated. In the first attempts the values found are often $\frac{1}{2}$ to $\frac{1}{3}$ per cent too high. In order to decide whether the homologues of phenol can be titrated alkalimetrically, the author experimented with the three cresols. The values obtained with ortho- and meta-cresol were rather uncertain, whilst in a solution of para-cresol the first drop of soda-lye produced a disturbing yellow colour. The method is not also applicable to pyrocatechin.

Volumetric Determination of Zinc.—L. Blum.—In order to remove manganese, if present, 50 c.c. of the solution to be examined are mixed with a few c.c. of bromine water, then with ammonia and 5 c.c. of Moldenhauer's mixture (which contains in 100 c.c. 5 grms. solid ammonium carbonate, 5 grms. ammonium chloride, and 10 c.c. ammonia). In the precipitate are found the iron, the manganese, and the alkaline earths; zinc and magnesium remain in solution.

A New Thermometer Scale.—F. Salomon (*Zeit. fur Angew. Chemie*).—Already inserted.

The Dispersion of Prism-Spectroscopes.—G. Guglielmo.—Already inserted.

Prevention of "Bumping" in Boiling Liquids.—E. Beckmann (*Zeit. fur Angew. Chemie*).—The author introduces into the heated surface thick pieces of wires (platinum, platinised wire). It is said that in such vessels sulphuric acid can be distilled without danger, and oxidations with alkaline permanganate can be effected without bumping.

Certain Forms of Densimeters.—E. Janisch (*Arch. der u. Math. Phys.*).—In these instruments equal degrees correspond with equal intervals of density.

A Pyknometer for Syrups.—K. C. Neumann (*Zucker Blatt. and Zeit. fur Angew. Chemie*).—This instrument has the form of an Erlenmeyer flask, with a high bottom, pressed in conically. In this manner a uniform and rapid cooling is effected.

An Instrument for Determining the Correction in Accurate Readings of the Mercurial Thermometer.—Ch. Ed. Guillaume (*Comptes Rendus*).

Washing-Bottle for Hot Water, Acids, or Ammonia.—A. Friedmann (*Stahl und Eisen*, x., 884).—The flask in place of the short tube is fitted with a three way piece, one end of which is connected with the blast, whilst the other end, when in use, is closed with the thumb.

A Spirting-Bottle.—R. Namias.—The author has constructed a bottle resembling that of D. H. Browne, in which a continuous blast does not need to be kept up with the mouth (*Stahl und Eisen*, xi., 239).

An Apparatus for Determining Melting-Points in a Liquid Bath.—R. Ebert (*Chem. Zeit.*, xv., 76).—For the details of this instrument we must refer to the original.

A Safety-Burner.—M. Lautenschläger (*Zeit. Angew. Chemie*).—A valve is inserted in the gas-pipe, which is held open by an electro-magnet whilst the flame is burn-

ing. If the flame is extinguished the current is interrupted and the gas-pipe is closed.

Enamelled Water-Baths with Ring Supports of Enamel.—B. Fischer (*Zeit. Angew. Chemie*).—Already inserted.

A Water Air-Pump Applicable as a Suction-Pump and a Blast.—Max Stuhl.—From a circular; it requires the accompanying illustration.

Water Air-Pumps of Aluminium Bronze.—(*Chem. Zeit.*).—The firm, Ehrhardt and Metzger, of Darmstadt, send out air-pumps of this material.

Improvements in Benzene and Spirit Lamps.—G. Barthel.—The construction of these lamps is shown in the accompanying figures.

The Purification of Mercury.—J. M. Crafts.—From the *Bulletin de la Société Chimique de Paris*.

The Preparation of Lackmoid.—Schaerges (*Schweitz. Wochenschrift Pharmacie and Chemiker Zeit.*).—Already inserted.

Separation of Manganese and Zinc.—Paul Jannasch and J. F. McGregor.—Already noticed.

Determination of Phosphorus in Crude Iron, Steel, and Iron Ores.—F. A. Emmerton.—This method is found in a work by A. A. Blair, "The Chemical Analysis of Iron," which we have lately had the opportunity of noticing.

Determination of Phosphorus in Iron and Steel.—Ch. Malet.—From the *Comptes Rendus and de la Société de l'Industrie Minérale*.—Already inserted.

Separation of Arsenic and Phosphoric Acids from Mercury, and Determination of Nitric Acid, Chlorine, and Sodium, in Presence of Mercury and Phosphoric or Arsenic Acid.—Konrad Haack. An inaugural dissertation (Meyer and Müller, Berlin).—Already inserted.

Isomeric Determination of Nitrates and Chlorates.—L. L. de Koninck and E. Nihoul.—This paper requires the accompanying figure of the complex apparatus employed.

Reactions for Distinguishing Tannin and Gallic Acid.—J. Napier Spence.—From the *Journ. Soc. Chem. Industry*.

Detection of Saccharin.—D. Vital (*L'Orosi*).—Already inserted.

MISCELLANEOUS.

Occurrence of Vanadium.—According to the *Chemiker Zeitung*, a considerable deposit of vanadium has been found in the Argentinian province, Mendoza.

A Laboratory Device.—Most practical chemists are painfully aware of the unsightly appearance of reagent bottles caused by the drops of the solutions running down the outside and crystallising thereon. This may be prevented by simply painting the rim with melted paraffin. Care should be taken to cover only the side of the lip—none should be put on the upper surface. This can be accomplished most easily by using a small hog-hair brush and a wax of low melting-point, such as is used for embedding sections. It will be found that besides preventing the solution trickling down the outside, it enables one to deliver the reagent easily in single drops without resorting to the plan of only partly withdrawing the stopper. *Ex-perto crede.*—R. E. B.

The Atomic Weight of Chrome.—C. Meineke.—The general mean result is Cr=51.94. This value agrees well with that of Rawson, 52.01, especially if we consider that if reduced to a vacuum it becomes 51.98.—*Zeitsch. fur Anal. Chemie*, xxxi., Part 1.

Process for Purifying Carbon Disulphide without Distillation.—A. Chenevier (*Bull. Soc. de Bord. and Chem. Zeitung*).—1 litre of the specimen is mixed with 0.5 c.c. of bromine and left at rest for 3 to 4 hours. The bromine is then removed by agitation with potassa-lye in slight excess or by means of copper turnings. If the liquid is still turbid, it may be rendered perfectly clear by agitation with a small excess of calcium chloride and filtration.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Medical, 8.30.
Society of Arts, 8. (Cantor Lectures). "Mine Surveying," by Bennett H. Brough, Assoc.R.S.M.
TUESDAY, 12th.—Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
Photographic, 8.
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WEDNESDAY, 13th.—Pharmaceutical, 8.
THURSDAY, 14th.—Mathematical, 8.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1690.

THE CHEMICAL CHANGES ATTENDING PHOTOGRAPHIC OPERATIONS.

I.—THE THEORY OF DEVELOPMENT IN RELATION TO THE ESSENTIALLY ELECTROLYTIC CHARACTER OF THE PHENOMENA AND THE NATURE OF THE PHOTOGRAPHIC IMAGE.*

By HENRY E. ARMSTRONG, F.R.S.,
Professor of Chemistry in the City and Guilds of London
Central Institution.

No pretension to be even a professional amateur photographer is made by the writer of these lines. At intervals extending over a considerable period he has exposed and developed plates in a conventional and rule-of-thumb manner, but about a couple of years ago an awakening of his photographic conscience took place, and he began to ask himself whether he had any true understanding of what he was doing? Finding that he had not, and that the text-books afforded but cold comfort, he bethought him that he was working in a manner utterly unworthy of a member of that fraternity which seeks to give its meaning to the watchword by which it is led—Science: "Knowledge co-ordinated, systematised, and arranged."

To-night he will attempt but a very general confession of the faith that is beginning to arise within him after much pondering over photographic literature, and after a couple of years of study and experience of the behaviour on development of plates exposed in the field at all seasons, and under a considerable variety of conditions, one chief object in view having been to arrive at the explanation of the controlling influence exercised by the restrainer, and the accelerating effect of alkali.

Thus much by way of preface. A prologue may be added to facilitate the explanation of points of fundamental importance.

In the year 1868 De la Rue and Müller described a new form of voltaic cell consisting of a cylinder of silver chloride cast around a silver wire as negative element opposed to a zinc rod as positive element, placed side by side in a tube containing a solution of a chloride—ammonium chloride being that ultimately preferred. (It is worth while noting that they speak of silver chloride as so poor a conductor of electricity that it may be regarded as an insulator, and that on this account it is necessary that the silver wire around which the chloride is cast should project through it into the solution. On the other hand, it is also noteworthy that even solid silver chloride may be electrolysed, and that directly its temperature is raised sufficiently to make it viscous, it is an exceedingly good conductor). In such a cell the silver chloride remains unchanged until the circuit is completed by joining the zinc and the silver by a conductor of electricity; immediately this is done a current passes, and simultaneously zinc dissolves and silver chloride becomes deprived of chlorine. Although ammonium chloride is used in the cell, in considering the nature of the interchanges it is permissible to assume that hydrogen chloride—one of the constituents of ammonium chloride—is the active agent; for, as will be shown later on, at the same time that hydrogen chloride is being withdrawn from ammonium chloride and used up, hydrogen chloride is being produced and converted into ammonium chloride, and as the two actions balance each other, it is unnecessary to consider them.

Supposing that silver, and not silver coated with silver chloride, were opposed to the zinc in the cell, the latter would dissolve as chloride; but hydrogen would be given off at the surface of the silver. In this case the current would rapidly fall off, the cell would become polarised in consequence of back action setting in between the hydrogen coating the silver and the zinc chloride, which would lose chlorine. As it is reversible, the change occurring under such conditions may be written—



i.e., the equation may be read either backwards or forwards. In the presence of silver chloride in contact with the silver, this back action or polarisation is prevented, no hydrogen ever being set free, as at the same time that the zinc combines with chlorine from the solution, an equivalent amount of hydrogen combines with chlorine of the silver chloride, and thus the amount of chlorine as ammonium chloride in solution is maintained constant. We therefore may represent the state of affairs in the cell before and after the current passes in the following manner:—

Zinc plate	$\begin{array}{c} \text{ClH} \\ \text{ClH} \end{array}$	$\begin{array}{c} \text{ClAg} \\ \text{ClAg} \end{array}$	Silver plate
Cell at rest.			
= Zinc plate	$\begin{array}{c} \text{ZnCl} \\ \text{ZnCl} \end{array}$	$\begin{array}{c} \text{HCl} \\ \text{HCl} \end{array}$	Ag (Silver Ag plate)
Cell in action.			

The electrical pressure developed in such a cell—its electromotive force, or E.M.F.—is about 1.05 volt; the theoretical value may be calculated in the following manner:—

It is known from thermo-chemical measurements that the dissolution in dilute muriatic acid ($\text{HCl} : \text{H}_2\text{O} = 1 : 200$) of sufficient zinc to displace 2 grms. of hydrogen would involve the evolution of 34,200 grm.-deg. C. units of heat.

If this amount of hydrogen and the equivalent amount of chlorine were to interact and form hydrogen chloride, 78,640 units of heat would be liberated; while by the interaction of the equivalent amounts of silver (216 grms.) and chlorine, only 58,760 units of heat would be liberated. Consequently, $78,640 - 58,760 = 19,880$ units of heat would be developed if the hydrogen, instead of being liberated, were to reduce silver chloride, and the total heat evolution resulting from the conversion of the zinc into chloride at the expense of the chlorine withdrawn from the silver chloride would be $19,880 + 34,200 = 54,080$ units. The corresponding E.M.F. is found by dividing by 46,000, a constant which need not be explained here; hence—

$$\frac{54,080}{46,000} = 1.18 \text{ volt.}$$

The difference between this and the observed value is attributable to the fact that the conditions for which the calculation is made are not precisely those which obtain in an actual cell; probably the zinc chloride is not fully hydrated in the electrical circuit, and the heat of formation of some less hydrated chloride should be taken for the purpose of the calculation.

The extent to which the electrolysis of silver and hydrogen chlorides takes place, i.e., the amount of zinc dissolving and of silver chloride reduced in the cell, depends on the resistance in the electrical circuit, since—

$$C = \frac{E}{R}$$

where C stands for current, E for electromotive force, and R for resistance. This is the well-known *Ohm's Law*; its importance in connection with photographic phenomena has been strangely overlooked.

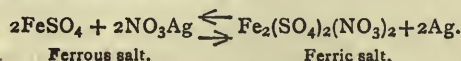
To apply this law to chemical changes, it has merely to be borne in mind that C may also be taken as meaning amount of chemical change, and it is scarcely necessary to point out that the most exact method of measuring an electrical current consists in determining the amount of

* From the *Journal of the Camera Club*, Conference Number 1892.

chemical change which the current produces by weighing the deposit of silver obtained on passing it through a silver nitrate solution. E, as before, is the electromotive force corresponding to the interchange, and R the resistance, not of the liquid as a whole, however, but of the circuit within which the interchange is effected, which may be quite a different thing, and unfortunately at present is beyond measurement.

It will be noted that the E.M.F. of the silver chloride cell is the sum of two E.M.F.'s, the one developed in the formation of zinc chloride from zinc and hydrogen chloride, the other in the reduction of silver chloride. In any case, in order that action may occur, it is essential that the change, on the whole, be one in which energy is set free; but this is not necessarily the case in all parts of the change when it is resolvable into parts. This is a consideration of primary importance in connection with the theory of development, and may be illustrated by the following examples:—Zinc readily dissolves in diluted sulphuric acid if coupled with a less positive conductor. Copper, however, does not, even if the acid be boiled; but copper dissolves readily enough if oxygen be passed into the heated diluted acid. Thermo-chemical measurement shows that while the dissolution of sufficient zinc to displace 2 grms. of hydrogen from sulphuric acid is attended with a liberation of energy expressed by the number 37,730 if represented in heat units, the dissolution of the equivalent amount of copper could only take place if energy were supplied to the extent of 12,400 heat units; but, as oxygen and hydrogen interact, forming water, with liberation of energy to the extent, measured in heat units, of no less than 68,360 units per 2 grms. of hydrogen, it becomes possible for copper to dissolve in sulphuric acid in presence of oxygen in a circuit containing copper, sulphuric acid, and oxygen, with development of energy equal to $68,360 - 37,730 = 30,630$ heat units: *i.e.*, a positive E.M.F. is developed in such a circuit.

In the old collodion wet-plate process, development was effected by means of silver nitrate left adhering to the plate on removal from the silver bath, and a reducing agent such as ferrous sulphate duly restrained by, say, acetic acid. When solutions of ferrous sulphate and silver nitrate are mixed, unless very dilute, a precipitate of silver is soon formed, but the amount precipitated always falls far short of the total amount of silver present, as the interaction is reversible.



The extent to which silver is deposited depends on the proportions used, the concentration, and the temperature; if the solution be sufficiently dilute and acid be present, no precipitation occurs. The exact function of the acid is not clearly determined, but probably in its presence atmospheric oxygen intervenes, and by acting in conjunction with it and ferrous salt, further promotes the dissolution of the silver, thus rendering reversal complete, *i.e.*, no chemical change is apparent. There can be no doubt that in the liquid the interchanges thus pictured occur within voltaic circuits, and that as no action is observed when acid is present, the algebraic sum of the currents in all these circuits is nil. It is to be supposed that on covering an exposed plate with such a solution, the image acts like the silver rod in the De la Rue-Müller cell, silver nitrate taking the place of the silver chloride, and ferrous sulphate that of the zinc rod in the cell: hence the silver is necessarily deposited on the image.

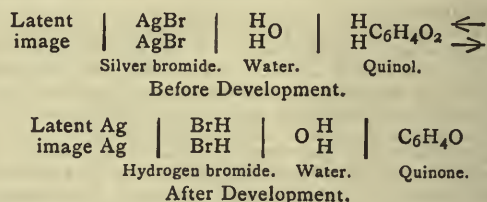
The growth of the image in silver therefore takes place mainly upwards into the solution in the case of a collodion wet plate, and only to a minor extent within the film; it appears probable that the silver haloid particles in the film in contact with the image are but little if at all affected, owing to the superior readiness with which silver nitrate is reduced, and the "weakness" of the developers used. It is very noteworthy that owing to the absence

from collodion of "active impurities," its use affords little or no opportunity for the occurrence of changes at points where light has had no action on the film: hence the brilliancy and sharpness of wet collodion pictures.

In considering the alkaline development process of modern gelatin dry plate photography, it would appear to be necessary to distinguish between methods in which the alkaloid ammonia, and those in which alkalies, either caustic or carbonated, are used. Even silver bromide is appreciably soluble in ammonia; consequently, in developing with the aid of ammonia, the image is in part formed from silver in solution. The extent to which this takes place depends chiefly on the amount of bromide added as restrainer, one result of adding this restrainer being to precipitate the dissolved silver haloid, or rather to prevent its dissolution by the ammonia. Probably it is to this peculiarity that the marked difference in results obtained by using ammonia and pyro is, at least in large part, attributable; and the same circumstance would favour the formation of an image not wholly composed of silver, *i.e.*, of a species of pigment.

All who have worked with pyro and ammonia know that the picture has properties which distinguish it from those obtained with developers in which ammonia is not used, and that the liability to certain peculiar kinds of fog is special to ammonia developers; this is probably attributable to the conjoint action of the dissolved silver and colouring-matter formed by oxidation of the developer.

When alkalies are used the image grows at the expense of the solid silver haloid with which it is in contact, just as the silver wire in the De la Rue-Müller cell grows at the expense of the silver chloride cast around it. The various developers used, like zinc, are all oxidisable substances; and just as the zinc by combining with chlorine enables the hydrogen of hydrogen chloride to withdraw chlorine from silver chloride attached to the silver wire in the cell, so the developer by laying hold of the oxygen of water enables its hydrogen to withdraw bromine from the silver bromide attached to the image on the photographic plate which has been exposed to light. Taking quinol (hydroquinone) as the type, the interaction may be expressed thus:—



Viewing the process in this manner the function of the alkali would seem to be to neutralise the acid as it is formed, or rather, to prevent acid ever being formed, thereby preventing a reversal of the interaction which otherwise would take place, owing to the attraction of silver for bromine and of quinone for hydrogen, on which account the equation given above is written as expressing a reversible change.

But the remarkable positive influence of alkali in hastening development, and the retarding influence of a bromide, such as potassium bromide, are in no way accounted for in the foregoing explanation.

As regards the alkali, its influence is probably at least in the main due to the fact that a silver haloid in presence of alkali and a reducing agent tends to undergo reduction, the metal of the alkali forming a compound with the halogen while the oxygen of the alkali forms water with the hydrogen of the developer. One of the products of this interchange is the alkali-metal haloid, and the interchange being a reversible one, its reversal is promoted by the presence of added bromide, and consequently less silver is deposited when the restrainer is present, thus:—



Provided it be assumed that the latent image is capable of acting in a manner corresponding to that in which the silver rod acts in the silver chloride cell, it is unnecessary to take its precise character into account. Yet to fully understand the relative importance of the various factors operating during exposure and development, it is necessary also to consider the nature of the photographic image. For an able statement and discussion of this and of very many other photographic problems, reference may be made to Meldola's "Chemistry of Photography" (Macmillan and Co.).

It is now generally admitted, Meldola says, that the invisible image is of the same composition as the darkened product of photo-decomposition of a silver haloid, and he inclines to the belief that this darkened product is an oxyhaloid compound of silver.

Mr. H. B. Baker, whose name is familiar to chemists through his remarkable observations on the incombustibility of carbon and phosphorus in dried oxygen, has for some time past been studying this subject with special care, and it may be here stated, on his authority, that when darkened silver chloride is treated with chlorine it gives off oxygen, and that water is formed when it is heated in dried hydrogen; these observations clearly indicate that the darkened substance contains an oxidation product, and confirm Hodgkinson's results, to which Meldola has drawn attention.

But if the arguments adduced in favour of the view that the invisible image is of the same nature as the darkened product be carefully examined, it will be found that they are by no means cogent. One object of this communication is to suggest that probably they are not, and further, that in an ordinary photograph there are perhaps two distinct latent images behaving differently on development, which may be conveniently spoken of as the *blue* and the *yellow* image. It is contended that the blue image is silver, and only the yellow a silver oxyhaloid. The action of light on silver haloids is apparently strictly comparable with that of an electric current—it is *electrolytic*; moreover, the effect of light would seem to be that of a very high electromotive force, and it would therefore overcome great resistance. It may be supposed that when exposed to the mis-called actinic rays—those at the blue end of the spectrum—in contact with a substance capable of appropriating bromine, *i.e.*, a depolariser, such as gelatin, and the products formed therefrom during ripening, silver bromide has its silver liberated. The development of the image thus formed has already been described; such an image would be the absolute counterpart of the silver wire in the De la Rue-Müller cell.

Lower down in the spectrum, in the yellow region, the silver bromide apparently undergoes electrolysis in some occult manner in a circuit which includes oxygen, and while losing some of its bromine takes up oxygen in place thereof.

In anticipation of the objection that if these two actions take place darkened silver haloid should contain both silver and silver oxyhaloid, and that apparently the former is not present in it, let it be remembered that when a moist silver haloid is affected by light, the halogen liberated in the formation of the oxyhaloid will attack the silver which it is here supposed results from the decomposition of the haloid by the blue rays, and will convert it into silver haloid. In a gelatin plate, however, halogen is taken up by the gelatin, &c., and thus the silver would be more or less protected; after a time, the gelatin having become saturated, the silver would tend more and more to become re-halogenised; in fact, it would entirely depend on the length of exposure whether

the image consisted of silver and silver oxyhaloid, or only of the latter.

On developing what is known as an over-exposed plate, which presumably is rich in oxyhaloid, the image apparently behaves very differently, according as only alkali is used in conjunction with the developer, or alkali and a bromide. It would seem probable that a silver oxyhaloid would resemble silver oxide in being very unstable, and that in contact with alkali and a reducing agent it would become resolved into silver haloid and silver, thus affording an image in silver, the growth of which, on continuing development, would occur in the manner previously explained. The decomposition of the oxyhaloid, like the change which occurs when solutions of silver nitrate and ferrous sulphate are mixed, would take place, so to speak, with a rush, and the image grow so rapidly that the picture would flash into view. One function of the restrainer is to prevent this sudden change; it would seem that under the conjoint influence of a bromide, alkali, and a reducing agent, the silver oxyhaloid is converted into silver haloid. The extent to which this change takes place, and the rate at which the picture gains in strength, would depend on the amount of bromide present, the relation which obtains between the amounts present of the several substances which act conjointly, the concentration, and the temperature; consequently the picture might, as is the case, be caused to grow at any desired rate.

In a gelatin plate there are always present substances tending to interact with the silver haloid in presence of alkali much in the manner in which silver nitrate and ferrous sulphate interact, and which promote the occurrence of the reduction of the haloid by the alkali and the developer already referred to. Such substances are kept under control by the addition of the restrainer. If, therefore, the development of an over-exposed picture be continued, fog is necessarily produced unless sufficient bromide be added to check the action of the reducing substances in the gelatin. For a similar reason it is desirable to use weak developers with plates which have had a very brief exposure. In such a case the image is so very faint that the difference between the unexposed and exposed portions of the plate is but slight—the value of R in the equation,—

$$C = \frac{E}{R},$$

is very nearly the same in the two sets of circuits. By using a developer which has no appreciable action on the unexposed plate, the latent image is slowly strengthened, and ultimately R is so much diminished that it becomes safe to use a stronger developer.

The development of pressure marks may be explained from the same point of view. Clearly there would be a diminution of resistance in the lines of pressure, and hence on application of the developer, circuits would be formed within the film in these lines, in which action would take place more readily than in the uncompressed parts.

Reversal by means of *thiourea*, with which we have been made familiar by Waterhouse, may also be referred to here. If it be supposed that the latent image is converted into a sulphur compound which is not developable, the action would be confined to the unexposed parts of the film which, sooner or later, always give way under the influence of alkaline developers. Complete reversal would thus be secured.

With reference to the sensitiveness of plates, the explanation at the end of the "prologue" of the influence oxygen exercises in promoting the dissolution of copper in diluted sulphuric acid is apposite. The sensitiser promotes the action of light in a precisely similar manner, it may be supposed; and it is clear that any degree of sensitiveness may be secured, according as the substance associated with the silver haloid, and which acts as depolariser by combining with the halogen thrown off from the haloid under the influence of light, is capable

of contributing more or less of the energy necessary to render the interchange one which would occur without any external E.M.F. being brought to bear.

Judged from the point of view here advocated, it would seem that there can be but very little difference between various developers when used under comparable conditions; at most the variation would arise in the rate at which development would take place. It does not appear probable that the character of the deposit would vary greatly in "grain" or colour. But, since in practice considerable differences are noticed, it is probable that not only in the case of pyro and ammonia, but also in others, the deposit does not invariably consist of silver alone.

In concluding this statement, attention may be called to the great opportunity for research of a by no means difficult character which photography affords. We want experiments made in a great variety of directions, but under much simpler conditions than heretofore adopted; the effects of monochromatic lights, and the influence of various pure substances as sensitisers in association with silver haloids, are especially important subjects to study.

Abney has shown that such a substance as a nitrite stops the action of the yellow rays: we want observations on the effect of such substances. Gelatin plates have been of great service to picture makers, but they are a great bar to scientific progress, as we can never know their exact composition, and we must return to the neutral medium collodion if we wish to gain definite information on matters such as have been referred to. Such experiments, moreover, should have great practical value, as the results may ultimately enable us to largely extend the applications of photography.

THE SCIENTIFIC ALLIANCE.

We have pleasure in calling attention to a movement which has sprung up in New York under this name, and which seems worthy of imitation elsewhere. According to our excellent contemporary *Science*, in March, 1891, six societies engaged in scientific research entered into a confederacy for certain well-defined objects. It is pointedly remarked that:—"The societies do not in any way sink their individuality or surrender any part of the management of their own affairs. Their union is merely in the way of co-operation for the advancement of science and for mutual encouragement, carried out through a central representative body known as the council, having advisory powers only. A monthly bulletin is issued, and is sent to every member, which contains an invitation to the members to attend the meetings of all the societies."

The associated bodies are the New York Academy of Sciences, formerly known as the Lyceum of Natural History; the Torrey Botanical Club; the New York Microscopical Society; the Linnean Society of New York; the New York Microscopical Club; the New York Mathematical Society.

It is not too much to say that a similar organisation might be useful in London. The combined influence of such a body might prove a check to the hostile movements alike of the Government and of so-called "advanced thinkers," who are ever on the watch to interfere with research. We need merely refer to the recent ukase touching methylated spirits, in which a foolish step was taken without the courtesy of consulting the Chemical Society and the Society of Chemical Industry. No society on entering such a combination would find its members treated as are the scientific members of our so-called "Literary and Philosophical Societies." Professor Meldola, by the temporary combined action of the London societies connected with the study of natural history, succeeded in defeating a project to lay waste a considerable portion of Epping Forest. It is therefore not too much to hope that by permanent co-operation much good might be done, or at least much intended mischief prevented.

THE SEPARATION AND DETERMINATION OF LEAD, SILVER, AND ZINC IN ORES COMPOSED OF GALENA AND BLENDE.

By EMILE AUBIN.

If we wish to separate and determine the lead, silver, and zinc by the wet way in ores composed of galena and blende, the attack with hydrochloric acid and the use of sulphuretted hydrogen for the separation of these metals renders the operations long and delicate, and the silver cannot be determined with precision. We have thought that it might be preferable to have recourse to fuming nitric acid to form an insoluble lead sulphate and soluble silver and zinc sulphates, which may be separated by filtration. The lead sulphate mixed with the gangue is then taken up and separated from the latter by means of a suitable solvent. Alkaline sodium tartrate, already indicated in analytical treatises, has given us the best results in this operation.

The following is the method which we finally adopted:—In a conical litre flask we act upon 10 grms. of the powdered ore with 50 c.c. of fuming nitric acid, heating the mixture to ebullition and evaporating to dryness on the sand-bath. It is re-dissolved in heat with 20 c.c. of nitric acid at 36° B., and when all the iron has passed into solution, the liquid is made up with distilled water to about 400 c.c. We agitate to re-dissolve the soluble sulphates and the nitrates, and then set the whole aside until the supernatant portion has become clear.

When the lead sulphate has been entirely deposited along with the siliceous gangue, the liquid is decanted through two plain filters previously brought to an exact equilibrium, and then placed one within the other. The deposit is brought upon the filter, completely washed with distilled water, and dried. The weight of the contents is then ascertained by separating the two parts of the filter and placing them on the opposite pans of the balance. Then the contents of the interior filter are let fall into a glass mortar and ground up with 30–40 c.c. of a hot solution of alkaline sodium tartrate at 20 per cent. The lead sulphate dissolves rapidly, and we judge that nothing remains but the gangue by the disappearance of the small white points which indicate the presence of the lead salt. The two filters, one within the other, are replaced in the funnel, and the contents of the mortar, including the insoluble portion, are decanted into the inter one. The filter is washed with distilled water until the filtrate has no longer an alkaline reaction. The siliceous gangue is dried and weighed. The difference of weight between the first and the second weighing represents the lead sulphate obtained from the ore. This weight multiplied by 0.6832 gives the lead in the metallic state. This result may easily be checked by re-precipitating the lead sulphate thus dissolved with an excess of sulphuric acid. The precipitate collected and washed upon a double filter, dried, and weighed, is equal in weight to the difference found in the previous determination.

The liquid which contains the silver and the zinc is made up exactly to 500 c.c. Of this we take 50 c.c., representing 1 gm. of ore, and determine the zinc by the ordinary method, i.e., precipitating the iron and alumina with ammonia, filtering, and adding to the filtrate ammonium hydrosulphate in excess to precipitate the zinc, collecting the deposit of zinc sulphide, re-dissolving it in hot hydrochloric acid, filtering, and precipitating the filtrate at the temperature of ebullition with sodium carbonate. The zinc carbonate is collected on a filter, washed, dried, and ignited in a wuffle. Its weight multiplied by 0.8025 gives the zinc in the metallic state.

For determining the silver the 450 c.c. of the original liquid are rapidly evaporated down in a capsule to 20 or 30 c.c. It is let cool, when there is formed a crystalline deposit, which is separated by decanting off the super-

out of linseed. 2. Salts which, whilst crystallising out from the mother-liquor, do not give off any heat: some of these salts take up heat whilst they are crystallising—the carbonates are instances of this kind. Precipitation; here is a kind of congelation or coagulation, and the atoms of carbon, silicon, and near-related elements impart such a property to some of their salts.

Before I end this paper, may I take the opportunity of fervently asking investigators to direct their attention to *uric acid*: for, according to Martignon (CHEM. NEWS, vol. lxii., p. 12), this acid must have very wonderful properties: the important part it plays in the animal organism points to this same fact.

Wimmerby, Sweden, March 21, 1892.

A QUICK AND RELIABLE METHOD FOR THE DECOMPOSITION AND ANALYSIS OF FERROCHROME.

By H. N. WARREN, Research Analyst.

THE analysis of ferrochrome is in itself no simple task, to say nothing of its previous decomposition. Samples containing high percentages of chromium are only slightly affected after long boiling with aqua regia,—hydrochloric or any other simple acids being entirely inadequate. True, a slow and imperfect decomposition may be brought about by fusing with acid potassium sulphate, and is often quickened by the addition of borax, but the results thus obtained are useless, inasmuch that the precipitates afterwards thrown down all contain large quantities of borates. The method, which is here described in brief, consists as follows:—

Having introduced a weighed quantity of the finely powdered substance into a convenient size flask, a sufficiency of strong H_2SO_4 is next added, and the action aided by a gentle heat. A copious evolution of SO_2 is almost at once evolved, and the heat is then increased until volatilisation of the H_2SO_4 is plainly perceptible; the whole of the ferrochrome is thus in the course of a few minutes brought into solution. To the solution thus obtained is added a few drops of HCl , the solution diluted to a known quantity having been previously filtered from the trifling carbonaceous residue, and an aliquot portion titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$ in order to ascertain the percentage of iron, a further portion being precipitated as chromic and ferric hydrates. From these data the percentages of both chromium and iron may be readily obtained; or if manganese or aluminium is considered worth allowing for, the precipitates are of course dealt with accordingly. A more complete and accurate analysis may be thus arrived at than by any hitherto known method. Analysts of iron works please take note.

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THE PROPERTIES OF AMORPHOUS BORON.

By HENRI MOISSAN.

AMORPHOUS boron, when pure, is a powder of a light maroon colour, which soils the fingers and may be agglomerated by strong pressure. Its specific gravity is 2.45. It is infusible at the temperature of the electric arc. If kept at a temperature bordering upon 1500° , in an atmosphere of hydrogen, it increases in density and is slightly agglomerated, though without becoming consistent.

Its electric conductivity is very slight; to measure it a pastille of boron is compressed between two plates of copper placed in a glass tube of known diameter. The resistance was then determined and the specific resistance

α was deduced from the formula $R = \frac{\alpha l}{s}$. We have

found for $l = 8.5$ m.m., and $s = 2.27$ m.m.c., $R = 300$ megohms, whence $\alpha = 801$ megohms.

In the air boron takes fire at the temperature of 700° . If strongly heated in a test-tube, and then thrown up into the air, it produces brilliant sparks. If heated in a current of oxygen it burns with a light so intense as to be insupportable. In a darkened room this incandescence appears green, but produces few chemical rays, thus it cannot be substituted for magnesium for photographic purposes.

In these various combinations the boron is not burnt entirely, for the layer of boric acid produces sets bound to the reaction. It combines with sulphur at 610° with a very beautiful incandescence; there is formed boron sulphide, which is decomposed by water with a production of hydrogen sulphide.

Selenium reacts at a higher temperature and without incandescence; there is produced boron selenide, which is decomposed by water with the disengagement of hydrogen selenides. Tellurium may be melted among amorphous boron without combination.

Boron takes fire in an atmosphere of dry chlorine at the temperature of 410° . The incandescence is very intense and boron chloride distils over. If the amorphous boron contains a small quantity of carbon or of carbon boride, a slight black residue is left in the boat. At the same time there are deposited in the tube traces of magnesium chloride and ferric chloride. Bromine combines with incandescence amorphous boron at about 700° , yielding boron bromide.

Bromine water slowly attacks amorphous boron at the ordinary temperature. If the boron contains magnesium boride the attack is much brisker, and there is a distinct evolution of heat. Pure boron is attacked more rapidly by a mixture of bromine, and of an aqueous solution of potassium bromide.

In a gas-furnace at 950° amorphous boron is not attacked by the vapour of iodine; combination does not even take place in a porcelain tube heated to 1250° . Iodine water has no action upon boron. Boron does not combine directly with antimony except at a very high temperature. At 900° in a current of pure dry nitrogen, boron yielded mere traces of a nitride after several hours. At 1230° combination takes place much more easily.

The vapour of phosphorus does not react upon amorphous boron at 750° ; it is the same with arsenic; antimony does not combine even if kept at its point of fusion. Carbon and silicon strongly heated do not appear to unite with boron. Still, under the action of the arc in an atmosphere of hydrogen, boron can combine with carbon, producing a carbon boride. The alkaline metals may be distilled over amorphous boron without producing a trace of combination. Magnesium, on the contrary, yields a boride at dull redness.

Iron and aluminium combine with boron only at high temperatures, whilst silver and platinum unite with it more readily. We are continuing in detail the study of the action of boron upon the metals.

Acids react energetically upon boron. At 250° sulphuric acid is reduced to sulphurous acid. Monohydrated nitric acid, in presence of an excess of boron, combines with incandescence. Phosphoric anhydride is reduced at 800° , with the liberation of phosphorus. Arsenious and arsenic acid are reduced at 800° , with the formation of a ring of arsenic. A hot solution of iodic acid liberates iodine in contact with boron. A mixture of boron and crystalline iodic acid, if gently heated, becomes incandescent, with the formation of intense vapours of iodine. Chloric acid in solution is reduced to chlorous acid.

The hydracids react less readily. Gaseous hydrofluoric requires to be heated to dull redness in order to act upon boron, and it is then split up into hydrogen and boron fluoride. Gaseous hydrochloric acid reacts only at a

bright red heat; its saturated solution has at 0° no action upon amorphous boron. Gaseous hydriodic acid reacts upon pure boron only at a temperature between 1200° and 1300° . Sulphurous acid gas is reduced by boron at a temperature below redness, the products being boric acid and vapours of sulphur.

Watery vapour does not react upon boron below redness, but as soon as incandescence has been reached at any point, the decomposition ensues with violence, boric acid being formed and hydrogen escaping.

At a temperature bordering upon 1200° carbon monoxide is reduced by amorphous boron, boric acid being formed and carbon deposited.

Melted silica is reduced by boron at the temperature of a good forge. Boron, if heated to dull redness in a tube of glass traversed by a current of nitrous oxide, becomes incandescent, yielding boron nitride and boric acid. Under the same conditions of temperature nitric oxide produces no result.

Metallic oxides are reduced more readily by boron than by carbon. If we heat, e.g., in a glass tube a mixture of cupric oxide and boron, the evolution of heat is so great that the glass melts immediately. Stannous oxide, litharge, oxides of antimony and of bismuth, are reduced at once if gently heated, and the entire mass becomes incandescent.

Lead dioxide, if ground up in a mortar with boron, detonates violently. Ferric oxide and cobalt oxide are reduced at a bright red heat. The alkaline-earth oxides are not attacked. Potassium hydroxide, if melted in contact with amorphous boron, produces a violent liberation of hydrogen.

The avidity of boron for oxygen may be demonstrated by means of a mixture of amorphous boron, sulphur, and potassium nitrate. This is a real gunpowder, which deflagrates below a dark red heat. We may also show this avidity by letting fall upon melted potassium chlorate some particles of amorphous boron. Combustion ensues with a dazzling light. This is a fine lecture experiment.

The action of boron upon certain metallic fluorides is very energetic. With the alkaline and alkaline-earth fluorides there is no reaction at a bright red heat. Zinc fluoride is reduced by boron at dull redness, yielding boron fluoride. Lead fluoride is reduced in the same manner, displaying a lively incandescence. If the quantity of boron is rather large the mixture deflagrates. Silver fluoride reacts in the cold, on simple contact in a mortar, with incandescence and detonation.

Boron does not attack the alkaline and alkaline-earth chlorides. Zinc and lead chlorides do not react at redness. Mercurous chloride mixed with boron yields about 700° boron chloride and vapours of mercury. Lead, zinc, cadmium, and copper iodides, if heated with boron in a glass tube, are not reduced, though the tin and bismuth iodides are readily reduced.

Potassium and sodium sulphates, if melted in a glass tube, are reduced by boron at a dull red heat. The incandescence is very intense, and there is produced an alkaline sulphide. Calcium and barium sulphates are reduced in the same manner, with incandescence. A part of the sulphur is volatilised, and there remains a metallic sulphide.

Although the affinity of boron for oxygen is very great, we may keep boron in a bath of an alkaline nitrate melting at 400° without any reaction. The attack begins only at the moment when oxygen begins to be evolved. With melting potassium nitrite the decomposition is attended with a great display of heat and light.

Sodium carbonate is reduced by boron at dull redness with a lively incandescence. For potassium carbonate the reduction is effected at a higher temperature. Calcium and barium carbonates are not decomposed. The arsenites and arseniates, as also the chromates, are reduced at dull redness, with incandescence.

We indicate a curious action which amorphous boron exerts upon a certain number of metallic solutions.

Amorphous boron reduces a solution of potassium permanganate in the cold, and the decolouration is complete on slightly raising the temperature. It reduces solutions of ferric chloride to the ferrous state. A solution of silver nitrate is reduced, with a production of very fine crystals of metallic silver. Palladium chloride is reduced in a few minutes at the common temperature. With platinum chloride the reaction commences in the cold, and is accelerated by a slight rise of temperature. If a few particles of boron are projected into a solution of gold chloride, reduction in the cold is instantaneous.

Boron combines less readily with the metals than with the non-metallic elements. It has a strong affinity for fluorine, chlorine, oxygen, and sulphur. It is a more powerful reducing agent than carbon and silicon, for at a red heat it expels oxygen from silica and carbon monoxide, and it will probably permit reductions more easily than those hitherto obtained with carbon.

Its action upon the metallic oxides easily reducible by carbon is very violent; it reacts very easily with a great number of salts, and it combines directly with nitrogen only at a very high temperature.—*Comptes Rendus*, cxiv., p. 617.

AUSTRALASIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SECTION B.—CHEMISTRY AND MINERALOGY.

ADDRESS BY THE PRESIDENT,
WILLIAM M. HAMLET, F.I.C., F.C.S.,
Government Analyst, N.S.W.

(Concluded from p. 175).

THE economical production of caustic soda would enable other wet process to be used, such as Ellershausen's wet process for the extraction of the precious metals from zinc ores. These latter give rise to grave difficulties in many parts of New South Wales, notably at the Barrier Ranges; in many cases the zinc is lost to the community for want of a suitable process of extraction. The method I refer to is one which can be economically worked in connection with the caustic soda manufacture. The zinc ore is mixed with 25 per cent of galena, if it does not already contain that quantity of galena, and after being crushed, is put in a reverberatory furnace and heated to a red heat, when from 35 to 50 per cent of caustic soda (the crude refuse from the soda works) is added. The whole mass fusing, the galena readily gives up its sulphur to the soda, and metallic lead is produced, which, with the gold and silver, sinks to the bottom, the sulphides of iron, copper, and zinc remaining in the slag. The lead is drawn off and cupelled, and the slag, on exposure to the air, rapidly crumbles to powder owing to the caustic soda present, which is afterwards removed by lixiviation, and can be used over again, while the metallic sulphides can be treated by the usual methods. The ore should previously be concentrated to remove quartz, as the soda would be wasted in forming silicate of soda and not recoverable. The late Mr. Wilkinson, my lamented friend, who drew my attention to this interesting process, held the opinion also that the ores of Broken Hill, Moruya, and Castle Rag could be successfully treated in this way.

In addition to the many forms of chlorinating processes, there remains for me to mention another, the principle of which is that the sulphur present in many sulphide ores may be subjected to a particular degree of oxidation in a reverberatory furnace, whereby the soluble sulphate of silver is formed; this is afterwards separated out by leaching with hot water, as already described; the silver being separated as metal, while the copper and iron compounds are left as insoluble oxides. This process, known as Ziervogel's, is particularly well suited to argentiferous pyrites carrying from 10 to 40 ozs. of silver per ton.

Another process of wet extraction has been lately patented by Dr. Storer, of Sydney, and Mr. Marsh, of Broken Hill, which may be briefly described as follows:—The ore is roasted in a reverberatory furnace along with limestone, the mass lixiviated with water, the zinc precipitated by magnesia as hydrate, which on filtration yields nearly pure zinc oxide.

Closely associated with the different processes I have brought before you, as well as with smelting operations generally, is the nature of the fuel and its suitability for metallurgical work. Mr. J. C. Mingaye, Assayer to the N.S.W. Government, has undertaken a thorough examination of the coals and cokes available in New South Wales, and finds them nearly equal in every respect to those of Europe and America, the exceptions being in the refractory nature of the ash of some specimens,—a defect, however, which is partly compensated for by their greater freedom from the undesirable elements phosphorus and sulphur.

The phenomenon of solution is, therefore, of world-wide interest, as we see its application in our arts, industries, and manufactures, as well as in the every-day acts of our lives. And all these changes, velocities, rotations, vortices, and precessions, even if we do not as yet perceive them, have been going on under our very eyes from the beginning; they are still going on in our laboratories and workshops, as well as in the great arena of nature. The truth is, that things constantly before us become so commonplace as to no longer awaken our interest as they did in the freshness of youth. Who has not observed the mixed feelings of awe and wonder when some friend comes, it may be for the first time in his life, to witness some natural phenomenon in a laboratory? Do we not find that such an one thus coming fresh upon the scene, untrammelled and free from preconceived notions, sets us thinking by some original and unanswerable question? There are not wanting among us some who talk of the narrowing tendency of the pursuit of Chemistry as a discipline of the mind. Such a view is totally at variance with fact and experience, since the great issues dependent upon a knowledge of Chemistry, and the enlarged conception of the universe gained by its study, places it in the front rank as an instrument of great educational value, and one best fitted to bring forward (*educer*) habits of observation and reflection.

One has but to think of the enthusiasm of a Liebig, a Faraday, and a Hofmann, and of the indomitable truth-seeking spirit which animated them, their sufficient reward being the inward satisfaction of having worked out, at first hand, an imperishable fact direct from Nature. To such as these comes the promise of the poet—

"Thy mind
Shall be a mansion for all lovely forms;
Thy memory be as a dwelling place
For all sweet sounds and harmonies."

Even such a mind as that of M. Renan has expressed the regret that he did not dedicate his life to chemistry instead of Oriental languages. Sir Henry Roscoe recently gave a reminiscence of the talented chemist, Dumas, who, after having declared that he had seen every phase of life—student, teacher, minister, professor, senator—but no work had he been called upon to perform had been so satisfactory, or had been looked back upon with such pleasure, as that of carrying on original work; and, he says, "If I had to live my life over again, I would not relinquish my quiet laboratory pursuits for all the splendour and influence of Court favour, or the turmoil and rewards of political life."

The advance of our science may be ascribed, not so much to the rewards offered by wealth, as to the disinterested love of truth on the part of the worker; for what man can pursue the even tenor of his way upon research work with the feverish spirit engendered by some pecuniary prize dangling before his eyes? The advance of Science may, moreover, be attributed to the greater freedom of the person, and to the full freedom of thought

that can be focussed at will upon everything relating to objective truth.

It was possible with our forefathers not to inquire, but it is fortunately impossible to stem the tide of free inquiry that, like the ether around us, pervades every thinkable subject. We remember, however, that the lives of our forefathers were overshadowed by the gaunt and chilling arm of Authority, which effectually barred the road to knowledge. *Tempora mutantur*; and with our freedom comes the intellectual growth and the desire to ascertain the truth as it may be revealed to us by the infinitely great and by the infinitesimal molecule. Let us not close our minds to the appreciation of the mutual relationship existing between the divisions of science known as Chemistry, Physics, and Astronomy; for what we know is as nothing to what we do not know and what still remains to be known. This may be a truism—sometimes it is half doubted. To me it seems like the literal truth, and that if we narrow our views to already half-conquered territory only, we shall be false to the men who won our freedom, and treasonable to the highest claims of Science.

And now, with the end in view, I feel conscious of having only touched the fringe of one phase of the all-absorbing subject of the nature of this beautiful universe; but, so far, you will, I think, agree with me in saying that the study of matter in its manifold aspects is not only worthy of our best energies, but full of promise for the future. The hard mechanical conceptions, accompanied by the dread born of an unreasoning superstition, formerly held regarding Nature, the irreverent and loose talk about "brute matter," and of dead motionless matter, is passing away. The "dead" matter is quickened, and is alive with movement. What was once taken for absolute rest and immobility is in a state of high tension and rapid motion, yet always in perfect harmony and in keeping with the orderly progress of the universe. Whether we peer out into the ethereal depth inlaid with suns, or whether we observe a crystal of potassium iodide dissolving in water, we have rolling worlds in the one case and the eddying molecule in the other, the gamut of the Universe being complete, from the protean carbon atom to the remotest so-called fixed star. Must we not, therefore, feel that the contemplation of such perfection of structure and such majesty of motion claims both our admiration and attention, and must lead us to recognise that in all around us we have—

Vox Dei in rebus revelata.

As with Lucretius, the gaze of the philosopher of the day is again centred upon the atom. The question still asked is, What are the atoms?

Ageless units in the amplitude of space,
Outlasting the ravage and the wreck of Time:
Now in a dewdrop distill'd from a rosebud;
Here in a crystal; there poised in a sphere
Evolving from fire-mist new worlds for the future
To vibrate anew the great clarion of Life.
These—these are the atoms.

THE FRACTIONAL ANALYSIS OF SILICATES.*

By F. W. CLARKE.

IN the course of some investigations upon the constitution of the natural silicates it was found that in most cases the empirical formulæ were capable of interpretation in various distinct ways, leading to different structural expressions of equal probability. In some instances there was available evidence, by means of which it was possible to choose between alternative formulæ; the final decision resting sometimes upon the association of minerals in nature, and sometimes upon the alterations which they undergo. Such data, however

* *Journal of the American Chemical Society*, xiii., No. 16.

are not always readily available, and even at their best they only establish presumptions in place of giving satisfactory proof. It became necessary, therefore, to seek for new data of an experimental kind, which should be analogous to the data used by the organic chemist in fixing the constitution of carbon compounds, and by their means to put the problem upon a more satisfactory footing.

Two difficulties were evident from the start. First, the impossibility, in the present state of our knowledge, of measuring the molecular weights of the silicates; and secondly, the lack of plasticity in the material under investigation. The first difficulty is still insurmountable; but the second is less formidable than it appeared at first, and the experiments presently to be described open up a feasible line of attack upon the outworks of the problem. The results are appearing in detail in a series of mineralogical papers by E. A. Schneider and myself, and only an outline of the chemical methods need be given in this communication. So far, the minerals studied belong mainly to the mica and chlorite groups, with a few other magnesium silicates like talc, serpentine, and olivine as accessories; and it remains to be ascertained whether the methods applicable to these compounds will fit other cases equally well. Theoretically, the outlook is favourable, but difficulties may exist which cannot be foreseen.

Of the minerals heretofore examined all but one, olivine, contain water. This may represent water of crystallisation, acid hydrogen, or hydroxyl in union with basic atoms, and the first problem is to discriminate between these several possibilities. To begin with, the relative stability of the water in each molecule gives a clue to its character; water of crystallisation being easily expelled at comparatively low temperatures, and water of constitution being more tenaciously retained. In each case, therefore, the temperature of dehydration was roughly ascertained; every mineral being heated to constant weight first at 100°, then at 250°, 300°, and finally at a full red heat. Whenever ferrous iron was present the total water was also determined directly, and so the errors due to possible oxidation during ignition were avoided. Studied in this way the vermiculite micas, kerrite, jefersite, and protovermiculite, gave exceedingly suggestive results, each mineral corresponding to an ordinary mica, plus three molecules of water of crystallisation, and with the alkaline metals of the original mineral equivalently replaced by hydrogen. Furthermore, the crystalline water fell sharply into two parts; two molecules being expelled at 100°, and the third being given off below 250°. Thus a mica having the composition $\text{Al}(\text{SiO}_4)_3\text{Mg}_3\text{KH}_2$ would yield by hydrous alteration a vermiculite represented by the formula $\text{Al}(\text{SiO}_4)_3\text{MgH}_3 + 3\text{H}_2\text{O}$, to which latter compound kerrite approximately corresponds. In the true micas and chlorites the water does not seem to break up into separate fractions upon mere heating, and, being stable up to or near redness, is to be regarded as constitutional.

Up to this point the work done presents no particular novelty, and involves no new modes of procedure. The fractional determinations of water, however, have a direct bearing upon subsequent experiments, and clear the ground for work of a more troublesome kind. Having evidence before us regarding the amount of hydroxyl in a given silicate molecule, the next problem is to determine its distribution and character. It may be united with silicon, representing unreplaceable hydrogen of the original silicic acid, it may be combined with magnesium in a univalent group —Mg—OH , or it may be linked with aluminum as —Al—OH or $\text{—Al}=(\text{OH})_2$. In its broadest aspect the problem is still far from complete solution, but at one point it has been attacked with some success, as follows:—

All of the silicates above mentioned as studied by us, except talc, are easily decomposable by aqueous hydrochloric acid. By dry hydrochloric acid gas, however, they are differently affected, and the differences seem to be

due to the character of the hydroxyl. Each silicate in turn was weighed out in a platinum boat, and heated to constant weight at a temperature of about 400° in a stream of the thoroughly dried gas. The temperature, it must be noted, is one at which the water of constitution was still retained by the minerals. Olivine, which contains no hydroxyl, was practically unattacked, although the aqueous acid decomposes it with great ease. Talc, the true micas, and the vermiculites, were not acted upon, or at most very trivially. Serpentine and the chlorides, however, were strongly affected; and from them, after the reaction, water extracted considerable amounts of magnesium chloride, in which the magnesia was estimated. In serpentine and ripidolite about one-third of the magnesia was thus removable; or, in other words, the magnesia was separated into two fractions, which presumably were differently combined. In these minerals the group —Mg—OH is almost necessarily assumed in any attempt to interpret their structure; and the amount of magnesia taken out as chloride was roughly proportioned to the quantity required by the simplest theory. That is, it seems probable that —Mg—OH in a silicate is converted by dry hydrochloric acid into a chlorhydrin group, —MgCl , the latter, by subsequent action of the gas being split off altogether as chloride, MgCl_2 . This is the simplest explanation of the phenomena; although the nature of the reaction is by no means proved, and a good deal of investigation into it is still necessary. At all events, as regards the magnesium silicates of the groups studied, the new reaction appears to be a legitimate test for —Mg—OH , even though it may not be strictly quantitative. When action takes place the group is almost certainly present; when there is little or no action, its absence may fairly be assumed.

(To be continued.)

NOTICES OF BOOKS.

Chemistry in Space. From Professor J. H. VAN 'T HOFF's "Dix Années dans l'Histoire d'Une Théorie." Translated and Edited by J. E. MARSH, B.A. Oxford: Clarendon Press, 1891.

STRICTLY speaking, structural formulæ are intended not to show the respective positions of the various elements which make up a molecule, but merely the relations existing among them. Still, in the minds both of their advocates and of those who reject them, there has lurked half unconsciously a notion that these graphic formulæ could or should to some extent shadow forth the constitution of a molecule could we view it with the requisite magnifying power. Hence, we have occasionally heard complaints concerning the folly of representing bodies of three dimensions upon a plane surface. The avatar of "chemistry in space," of the attempt to exhibit the manner in which the atoms of compounds are really grouped together, may therefore justly be hailed as a step in the right direction. At the same time, it is a most difficult step, which without extreme circumspection will expose us to the risk of going astray. For the present, the chemists who have initiated this advance are exceedingly cautious. They have not made any wide-reaching assumption, but have merely taken up the hypothesis of the "tetrahedral carbon atom." The theory in question originated, as we are told, independently and simultaneously in France and in Holland. M. J. A. Le Bel, in November, 1874, read a memoir before the Chemical Society of Paris on "The Relations which Exist between the Atomic Formulæ of Organic Bodies and the Rotatory Power of their Solutions." He reminded the Society of the correlation between molecular dissymmetry and rotatory power. Prof. Van't Hoff published, in the Dutch language, in September, 1874, a "Treatise on a System

of Atomic Formulæ in Three Dimensions, and on the Relation between Rotatory Power and Chemical Constitution." Here, therefore, identical conclusions seem to have been reached substantially by following the same train of thought. This pamphlet soon appeared in a German version, and, as it is here remarked, received two diametrically opposite criticisms from two chemists of recognised eminence. The two authorities in question were Wislicenus and Kolbe. The critique of Kolbe was not merely hostile, but contemptuously hostile. His motive was a doubt of the possibility of ascertaining the true arrangements of the atoms in a molecule, or, at least, of knowing positively whether our interpretation was correct or otherwise.

The author shows that this theory throws a valuable light upon the phenomena of isomerism.

In the chapter on the monatomism of compounds we find that, according to Pasteur and Le Bel, an inactive compound may be converted into one either dextro-rotatory or lævo-rotatory by the action of organisms.

We hope that "chemistry in space" will be thoroughly and carefully worked out. It has already obtained recognition so far that it no longer need fear the "conspiracy of silence."

The Year-Book of Science. Edited, for 1891, by Prof. T. G. BONNEY, D.Sc., LL.D., F.R.S. Small 8vo., pp. 473. London and Melbourne; Cassell and Co., 1892.

WE have here an annual built on almost the same lines as a defunct publication of very similar title; but the present work is a very decided advance on its fore-runner. Its subject-matter is gleaned, not from stray newspaper paragraphs—canards, distortions, or at best exaggerations of the truth—but from writings of specialists, as found in the Transactions of leading Academies and Societies, or from established scientific journals. Hence its contents are trustworthy.

The editorial preface contains much that is interesting. Says Dr. Bonney: "The increasing technicality of the terminology employed is also a serious difficulty. It has become necessary to learn an extensive vocabulary before a book in even a limited department of science can be consulted with much profit." This is too true. It has often struck us that one great advantage which the German student has over his English contemporary is that the former encounters technical phraseology built up out of his native tongue, whilst the latter has to grapple with a terminology intended to be Greek. It is humiliating to find an eminent official *savant* in one moment protesting against the predominance of classical studies in our colleges, and in the next engaged in the wholesale coinage of technical terms which only a Greek scholar can hope to understand. Odd-toed or even-toed are quite as precise as perissodactylate and artiodactylate, and very decidedly more concise.

The editor and his coadjutors seem to have experienced some difficulty in deciding how much ground should be covered. However this may have been, they seem to have come to a happy decision. The boundary-line between Science and technical applications seems to us distinct enough. If engineering and photography were admissible, why not medicine? Mathematics may possibly yet come to be regarded as a method, rather than as a science. The admission of metaphysics would be gravely to be deprecated.

As regards the various subjects, it seems to us that too great space has been conceded to organic chemistry, which is generally interesting only to the specialist.

Under "Animal Biology," we miss a sub-section on taxonomy and animal geography, corresponding to the sub-section "Systematic and Geographical Botany." Such a department would doubtless prove exceedingly interesting to the educated outsider. Among the subdivisions of the section on "Biology (Botanical)," we find one headed "Morphology and Biology of Plants."

We feel curious to know the exact sense in which the term "biology" is here to be taken. It cannot be meant as a synonym for physiology, according to the usage of some Continental authorities, since there follows a sub-section on vegetable physiology.

The section on Meteorology is exceedingly interesting. We particularly notice the alarming conclusion arrived at in *Ciel et Terre*—which certainly agrees with our own observations—that a cold winter has never been followed by a very hot summer, and that in the great majority of cases the summer following a severe winter has been cold. Hence we have a poor prospect for the ensuing season.

The work altogether should find a good opening, not merely among intelligent outsiders, but should prove a boon to scientific men, since they find themselves more and more in the position of "outsiders" in every department but their own.

A New Course of Experimental Chemistry, including the Principles of Qualitative and Quantitative Analysis; Being a Systematic Series of Experiments and Problems for the Laboratory and Class Room. By JOHN CASTELL-EVANS, F.I.C. London: Thomas Murby.

THE author admits in his preface that if he had simply added another to the long array of chemical text-books much ingenuity would be needed to justify the proceeding; but he considers that "something was wanting" which no existing manual or collocation of manuals could supply; that there was "something radically wrong in the usual way of teaching chemistry, &c." The something wanting he has in this book endeavoured to supply. We certainly cannot undertake the prolonged task of comparing all the existing manuals with that of Mr. Castell-Evans, and of pointing out if and where they fall short, and if, and how, the present author has avoided their errors. We may, however, venture to say that three at least of the existing short text-books—we names of which, of course, we may not mention—have done, or are doing, good service. Further, unless our memory is greatly at fault, not a few of the authors of other manuals, manualettes, guide-books, handbooks, and text-books assert, each in turn, that the existing works are defective, and that there is pressing need for improvement. The "guiding idea" of the present work is excellent. It is designed "not to furnish the student with a knowledge of chemistry, but to help him to acquire that knowledge in the most thorough and scientific manner." Nothing could be better. Mr. Castell-Evans has sought to produce "not a collection of facts, but of methods and means of discovering facts, and of drawing conclusions from them." If the author teaches chemistry in this spirit, his pupils may be congratulated.

We are further told that "since this work has been in the publisher's hands, the British Association has appointed an unusually strong committee to inquire into the methods adopted for teaching chemistry." Surely the answer to such an inquiry would not be very far to seek. Let them give in their formal protest against the examination system, with its appendages of "payment by results" (falsely so-called), and of the "grant-earning standpoint." Here, we are sorry to find, the author does not go with us in rejecting the system which tends to assimilate Britain with China. An accompanying table is said to "cover the honours degree in chemistry of the London University, Oxford and Cambridge Local, and South Kensington Examinations. We would earnestly beg the author to reflect whether our present system of studying with reference to some examination or other is not a fatal mistake.

Appointment.—Mr. F. J. M. Page, B.Sc., F.I.C., has been appointed to the Chair of Chemistry and Physics at the London Hospital rendered vacant by the death of Dr. C. Meymott Tidy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 13, March 28, 1892.

Attempt at a Theory of the Production of the various Vegetable Galls.—A. Laboulbène.—The chief cause of the production of galls consists in liquids emitted by galligenous animals and plants.

Temperature of the Sun.—H. Le Chatelier.—The author ascribes to the sun the effective temperature of 7600°, the error in either direction not probably exceeding a thousand degrees.

On a Lamp without Flame obtained with Coal-Gas.—F. Parmentier.—If a thin extended platinum wire is rendered incandescent with a Bunsen burner, or any other burner not producing a luminous flame, and the gas is suddenly turned off and not turned on again until the wire has fallen below dull redness, the platinum returns very rapidly to dark redness and then to bright redness. If the wire has been placed at about the half height and outside the zone where the blue cone is formed when the jet is kindled it always re-lights itself. If the wires instead of being stretched out are rolled up in close spirals we obtain anew a bright incandescence of the platinum and a re-ignition of the gaseous mixture. With thick platinum wires the experiment rarely succeeds.

The Fixation of Iodine by Starch.—G. Rouvier.—Starch may fix iodine without it being necessary to take for 4 atoms of iodine 1 mol. of hydriodic acid or of an iodide.

The Determination of Fluorine.—Ad. Carnot.—This paper will be inserted in full.

Bromised Aldehyds and Acetones resulting from the Action of Bromine upon the Alcohols of the Fatty Series.—A. Etard.—The action of bromine upon the alcohols of the fatty series enables us to obtain in abundance the bromo-aldehyds and acetones, the preparation of which has hitherto been impracticable.

Propylamines and Some of their Derivatives.—F. Chancel.—In order to obtain pure propylamine it is necessary to use oxalic ether, which gives dipropylamide. On pouring oxalic ether into a mixture of about equal volumes of monopropylamine and water, there is immediately a precipitate of dipropylamide. But if the oxalic ether is added by small quantities, and the temperature is prevented from rising, there are formed monopropylamine oxalate and propylloxamate. Propylamido-acetic acid is prepared by the action of monopropylamine upon ethyl bromacetate.

Certain Reactions of the Isomeric Amido-Benzic Acids.—Oechsner de Coninck.—Orthoamidobenzoic acid dissolves with the aid of heat in ordinary nitric acid, giving a garnet-red solution, then the tint rapidly turns to a dark brown. The meta- and para-isomers give similar colourations, but the para-compound is most resistant against nitric acid. Fuming nitric acid strongly attacks the ortho-amidobenzoic acid in the cold; the solution is a deep brownish-red. If distilled water is added it becomes red by transmission, and reddish-brown by reflection. It soon becomes turbid. The meta-acid is also strongly attacked, forming a red solution; on dilution with distilled water the solution becomes of an orange-red both by reflection and by transmission, and there is no turbidity. The author has in like manner examined the reaction of the three isomeric acids with aqua regia, with hydrochloric acid, dilute and concentrated, and with sulphuric acid.

Two Fluorhydrines of Glycerin.—Maurice Meslani.—Gaseous allyl fluoride reacts with ease upon bromine,

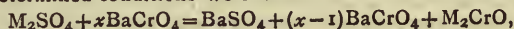
giving rise to a dibromfluorhydrine, $C_3H_5FBr_2$. With chlorine it yields under the same conditions a dichloro-hydrofluorhydrine, $C_3H_5FCl_2$. These compounds are liquids, endowed with great stability, and do not attack glass even at temperatures much above their own boiling-point.

Speed of the Decomposition of the Diazo-Compounds.—J. Hausser and P. Th. Müller.—A mathematical paper, not admitting of useful abstraction.

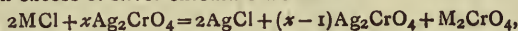
Revue Universelle des Mines et de la Metallurgie.

Series 35, Vol. xvi., No. 1, October, 1891.

New Process for the Determination of Soluble Chlorides, Bromides, and Iodides.—L. L. de Koninck and E. Nihoul.—In 1886 M. Quantin published a method for the determination of sulphates based upon the reaction between these salts and barium chromate. Under certain determined conditions we obtain—



M representing a monovalent metal. The barium sulphate and the excess of barium chromate are eliminated, and the soluble chromate formed is then eliminated. As the quantity of the latter formed is molecularly proportional to that of the sulphate, this determination enables us to calculate the weight of the sulphate contained in the substance under analysis. It seemed to us that an analogous method might be applied to the chlorides. It is known that silver chromate reacts rapidly with the alkaline chlorides to form silver chloride and a soluble chromate. If we treat a neutral solution of chloride with an excess of silver chromate we have—



the quantity of soluble chromate formed being proportional to that of the chloride. It is only necessary to remove by total or partial filtration the excess of insoluble chromate, and to determine the chromate contained in the liquid to obtain by calculation the quantity of chloride to be determined. For the determination of the soluble chromate formed the authors use the method of Zulkowski improved by Grismer, i.e., by means of hyposulphite with the intervention of potassium iodide and in presence of sulphuric acid. For preparing silver chromate they weigh two portions of silver nitrate and neutral potassium chromate, both pure, so that there may be 7 parts of silver nitrate to 4 of chromate. The two products are dissolved separately, and the two solutions are mixed, washed by decantation, and preserved under water in the absence of light. Potassium dichromate must not be used. The process consists in agitating with the solution of chloride an excess of silver chromate, filtering, washing, and determining in the filtrate, to which are added the washing-waters, the soluble chromate formed by the iodometric method. To 1 atom of chlorine there correspond 3 atoms of iodine, and consequently 3 mols. of hyposulphite. As regards the precautions necessary we recommend:—1. To use only silver chromate perfectly pure, and which has been preserved under water in the dark. 2. To operate only with perfectly neutral solutions. If the solution is slightly acid it may be neutralised by means of pure calcium carbonate. If the solution is alkaline it must be neutralised with dilute nitric acid, an excess of which may again be neutralised with calcium carbonate. 3. The known precautions for the iodometric determination of chromate must also be taken. An excess of alkaline sulphate should not be taken. The determination of bromides and iodides is effected exactly in the same manner as that of the chlorides. The precipitate of silver bromide or iodide often passes through the filter, but this fact does not interfere with the titration of the chromate.

Carbon Monoxide and Nickel, and its Application to the Metallurgy of this Metal.—L. Mond.—The substance of this paper is to be found in the CHEMICAL NEWS for August 28, 1891.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 1.

Detection of Isocholesterine.—E. Schulze (*Zeit. für Phys. Chemie.*—Already inserted).

The Saponification of Fats and Esters.—A. Kosel and K. Obermaier.—This paper will be inserted at an early opportunity.

Determination of Tannin.—S. J. Hinsdale.—From the *CHEMICAL NEWS*. See also R. Koch in *Dingler's Journal* (280, 141), and Whitely and Wood (*Journ. Soc. Chem. Ind.*).

Examination of the Air at Breweries, &c., for Micro-Organisms.—P. Lindner (*Wochenschrift für Brauerei*).—Already inserted.

Determination of Salicylic Acid in Beer and Similar Liquids.—H. Elion.—About 100 c.c. of the sample, after the addition of a little sulphuric acid, is shaken out with 2 or 3 vols. of ether. The salicylic acid is then withdrawn from the ether with small quantities of water, to which a little caustic alkali is added, and the aqueous solution thus obtained is neutralised with hydrochloric acid. In presence of salicylic acid this liquid gives the well-known colouration with ferric chloride.

Determination of Alumina in Wine.—L. Hôte.—From the *Comptes Rendus*.

Examination of Spirits.—The official regulations adopted by the Swiss Government.

Detection of Preparations of Cochineal in Sausages.—A. Klinger and A. Bujard.—The sample, finely minced, is extracted in a boiling mixture of equal parts of glycerin and water. If a preparation of cochineal is present the solvent takes a decidedly red colour. When cold it is filtered, and if but little colouring-matter is present additional 20 grms. of sausage are digested with the filtrate. The clear solution is examined spectroscopically.

Determination and Examination of Fats.—A collection of notes on oils and fats which will be abstracted by opportunity.

On Weighting Leather.—W. Eitner (*Der Gerber*).—Already inserted.

Action of Potassium Fluoride upon Anhydrous Chlorides. Preparation of Anhydrous Nickel and Potassium and Cobalt and Potassium Fluorides.—C. Poulenc.—M. Güntz in his thermic researches on the compounds of fluorine with the metals, has shown that in the action of hydrofluoric acid upon potassium chloride the thermic maximum always corresponds to the fluoride of a fluoride of the formula $KF.HF$. Hence the author concluded that in this manner there might be obtained anhydrous double fluorides of the formula $KF.MF$. In this manner a number of such compounds have been obtained. He describes at present two, the potassium-nickel and the potassium cobalt fluorides. The former body is slightly soluble in water, scarcely soluble in methylic and ethylic alcohols, and insoluble in amyl alcohol, in benzene, and in oil of turpentine. Its specific gravity is 3.27. Hydrofluoric acid dissolves it in the cold, as also do hydrochloric and nitric acids, its solubility in which increases with the temperature. Sulphuric acid attacks it very slowly at common temperatures, but more rapidly in heat, converting it into sulphate, with elimination of hydrofluoric acid. Ammonia, in the presence of this salt, gradually takes a violet-blue colour. If heated in presence of air this fluoride is converted into nickel oxide, green, and well crystallised, and into potassium fluoride, which escapes. It is reduced by hydrogen at a red heat. Potassa and the alkaline carbonates in fusion convert it into nickel oxide and alkaline fluoride. Cobalt potassium fluoride, $CoF_2.KF$, behaves with solvents in the same manner as the nickel compound. Its specific gravity is 3.22.—*Comptes Rendus*, cxiv., No. 13.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"The Chemist."—I have *The Chemist*, vols. 1 to 7, 1840-46; vols. 1 to 4, New Series, 1849-53; vols. 1 to 5, New Series, 1853-58. Were there any volumes published for 1847, '48, and '49? I have in several cases seen bound up with vol. 5, 1857-8, the first two numbers of vol. 6. Is this merely a coincidence? If not, I should like to know how much longer the journal ran.—J. CUTHBERT WELCH.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Meteorological, 7.

Microscopical, 8.

THURSDAY, 21st.—Chemical, 8.

FRIDAY, 22nd.—Quekett Club, 8.

NEW PUBLICATIONS.

THE TANNINS. a Monograph on the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astrings, with an Index to the Literature of the subject. By HENRY TRIMBLE, Ph.M. Vol. I., crown 8vo., cloth. 10s. 6d.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1691.

ON THE APPLICATION OF A HYDROGEN FLAME IN AN ORDINARY SAFETY-LAMP TO THE DETECTION AND MEASUREMENT OF FIRE-DAMP.*

By FRANK CLOWES, D.Sc. (London),
Professor of Chemistry, University College, Nottingham.

IN a former paper (*Roy. Soc. Proc.*, vol. 1., p. 122) an apparatus was described, in which the appearance of the "cap" over the flame of a safety-lamp could be observed and measured when the lamp was exposed to definite mixtures of air with methane or fire-damp. The relative sensitiveness of different forms of lamp, and of different flames, when they are applied to the detection and measurement of "gas," was thus readily ascertained. It was stated that the flames of colza oil, rape oil, mixed oils, benzoline, methylated spirit, and hydrogen had been experimented upon; and that the non-luminous flames producible by benzoline, alcohol, and hydrogen far excelled the more or less luminous oil flames in their power of indicating low percentages of inflammable gas or vapour in the air. It was further found that the delicacy of the test was much increased by grinding the inner surface of the back of the glass cylinder of the lamp, so as to destroy its reflecting power.

Ashworth's modified benzoline safety-lamp was especially referred to as an efficient lamp both for lighting and for gas-testing. The brilliant illuminating flame gave a forward light equal to one miner's candle. When it was reduced in size by drawing down the wick it became blue and non-luminous; and when it was viewed in this condition against the ground glass surface, or, better still, against the dead-black background produced by smoking the interior of the lamp glass at the back, a distinct flame cap, 7 m.m. in height, was seen in air containing only 0.5 per cent. of methane or fire-damp. The height, density, and definition of the cap over this flame were found to increase pretty regularly as the percentage of "gas" in the air was augmented. The efficiency of this lamp for lighting and testing is thus placed beyond doubt.

In continuing the experiments described in the former paper, however, a comparison of the "caps" produced by the flame of this lamp with those produced by a small alcohol flame and a small hydrogen flame showed that the latter flames were more sensitive as gas indicators than that of the benzoline lamp. Thus, when an alcohol and hydrogen flame, each 10 m.m. in height, were introduced, together with the small blue benzoline flame, into the testing chamber, which was filled with air containing 1 per cent. of coal-gas, flame caps of the following dimensions were obtained:—

Hydrogen	27	m.m.
Alcohol	19	"
Benzoline	7.2	"

It is true that the benzoline flame employed in this experiment was much smaller than the two other competing flames. But it must be remembered that the benzoline flame is necessarily small when it is employed for gas-testing, since, if its dimensions are increased, it becomes luminous, and renders the pale "cap" invisible. And one of the principal advantages of the alcohol and hydrogen flames consists in their remaining non-luminous, even when they are made of large

dimensions; the greater surface and higher temperature of their larger flames producing, therefore, much larger and more visible "caps" than is possible with a small benzoline flame.

It will be seen from the results of the experiment just described that the hydrogen flame has the advantage over the alcohol flame in the dimensions of the "cap" which it yields. But by prolonging the test, another advantage of the hydrogen flame over its rival was ascertained. The two flames were allowed to burn side by side in the chamber, charged with air containing 1 per cent. of coal-gas for over thirty minutes. Throughout this protracted test both the hydrogen flame and the "cap" above it remained unaltered in size and appearance. The alcohol flame and its "cap," however, steadily diminished in size; after five minutes the height of the cap had fallen from 19 m.m. to 12.5 m.m., and after another interval of five minutes the height of the cap was reduced to 6.5 m.m.; and thirty minutes after the beginning of the experiment the flame was spontaneously extinguished. This result seems to indicate that the alcohol flame is much more sensitive to the influence of the presence of products of combustion, and to deficiency of oxygen, than the hydrogen flame is: the difference is possibly due to the much smaller quantity of oxygen required by the hydrogen flame for its combustion.

Alcohol Lamps.—The possibility of producing large and distinct "caps" when testing by means of an alcohol flame for low percentages of "gas" in air was taken advantage of by G. Pieler in 1883 to produce the most sensitive form of safety-lamp for gas-testing yet invented. The Pieler lamp is a large Davy lamp, burning alcohol from a circular wick, which yields a large flame, 30 m.m. in height. When the lamp is used for testing even the feeble light of this flame is shielded from the eye, so as not to interfere with the perception of the "cap." Experiments with this lamp in known percentage proportions of "gas" and air have been described by several observers, and their results were fully confirmed by a series carried out in the test-chamber. The "caps" obtained were as follows:—

0.25 per cent. of methane gave a 30 m.m. cap.	
0.5	65
0.75	75
1.00	90

Indeed, the flame of this lamp is so sensitive that when the proportion of methane in the air reaches 1.75 per cent. the "cap" touches the top of the gauze of the lamp, and with a somewhat higher percentage of "gas" the enlarged "cap" completely fills the interior of the gauze.

Practical men, who have used this lamp, seem to feel some doubt as to its perfect safety in the mine. But their main objection is that the alcohol flames are non-luminous, and accordingly a second lamp must be carried for lighting purposes when the Pieler lamp is employed for gas-testing.

Attempts have been made to obviate the inconvenience of carrying two lamps by constructing a safety-lamp with two reservoirs. One of these would contain oil, and the other alcohol. Each would be supplied with a wick in the ordinary way. By raising or lowering one wick or the other a luminous oil flame for lighting purposes, or a non-luminous alcohol flame for gas-testing, should thus be obtained at will within one and the same lamp; the flame being passed from one wick to the other, as may be required. Practical difficulties arose in the use of this composite lamp, which have prevented its adoption.

Hydrogen Lamps.—Pieler was aware of the advantage secured by employing a hydrogen flame for gas-testing. Owing to the difficulty, however, of adapting a hydrogen supply to a portable safety-lamp, he recommended that samples of air from the mine should be brought to the surface, and tested by a hydrogen flame burning from a

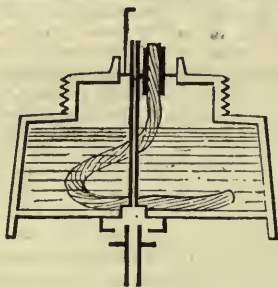
* A paper read before the Royal Society.

chemical generator, the apparatus being a fixture in a testing-room situated near the pit's mouth.

Since, however, hydrogen gas is now obtainable at small cost, compressed in light steel cylinders, it has been found possible to furnish a supply of the gas to a jet inclosed in an ordinary safety-lamp.

The lamp is so constructed that oil or benzoline may be burnt in the ordinary way from a wick when the lamp is to be used for lighting purposes, the wick being drawn down so as to produce a non-luminous flame, and this yielding caps in gas-testing when proportions of gas exceeding 3 per cent have to be looked for. When proportions of gas less than 3 per cent are to be looked for and estimated the hydrogen gas is introduced by a metal jet fixed close to the wick; the gas at once kindles. The wick is then drawn down until the oil flame is extinguished, and the cap is looked for over the hydrogen flame. A cap is easily seen over this hydrogen flame when only 0.25 per cent. of gas is present. When the illuminating flame is required the wick is again pushed up, and kindled by the hydrogen flame. The supply of hydrogen may then be withdrawn. The oil flame and the hydrogen flame are thus made to supplement one another in the same lamp in gas-testing.

The hydrogen is at present supplied from a small steel cylinder, 3 inches in diameter by 8 inches in length, and weighing 4 pounds. The cylinder when fully charged contains 4 cubic feet of hydrogen. This supply lasts for many tests, since when the flame is kept burning continuously at the ordinary height of 10 m.m. it consumes only 1 cubic foot of gas in about four hours. A regulator may be adapted to the neck of the cylinder, but it has been found that a very delicate valve in the neck of the cylinder serves to adjust the stream of gas with ease without the intervention of any regulator.



The cylinder is slung in a leather case by a strap across the shoulder. A flexible tube from the nozzle of the bottle connects the bottle with a little flanged metal nozzle, and this can be attached to an opening in the bottom or side of the oil reservoir of the lamp. The hydrogen is thus supplied to a copper tube of fine bore, which passes through the reservoir, and terminates on a level with, and close by, the top of the wick. Before the hydrogen is fed into the lamp it is gently turned on and allowed to sweep the air out of the flexible tube; connection is then made with the lamp, and by careful adjustment of the valve of the bottle the flame is made of the required size. The aperture in the lamp for introducing the hydrogen is closed by an automatic valve when the hydrogen is not in use.

Several series of measurements of "caps" were made over the hydrogen flame of this lamp in the testing chamber. The flame was adjusted to a height of 10 m.m. by viewing it through a metal diaphragm, containing a hole 10 m.m. in diameter, and held outside the lamp; or by making its tip level with the top of an upright wire fixed inside the lamp, and near the burner. A glass cylinder extra height (90 m.m.) was fitted into the Ashworth lamp, and a dead-black background was produced by smoking a broad strip of the internal surface of the internal surface of the back of this glass with a wax taper. The blackened glass not only gave a surface

against which pale caps were easily seen, but the dead surface prevented perplexing reflections giving ghosts of the true flame. The percentage of methane in the air in these experiments varied from 0.25 to 3, and the following heights of cap represent the average of a large number of fairly concordant readings:—

With 0.25 per cent. of methane, 17 m.m. cap.

"	0.5	"	"	18	"
"	1.0	"	"	22	"
"	2.0	"	"	31	"
"	3.0	"	"	52	"

In the 3 per cent mixture the tip of the cap disappeared in the opaque metal cylinder of the lamp above the glass. The hydrogen flame therefore became useless for measuring higher percentages, unless it was much reduced in size; but at this point the oil flame is competent to take up the indications with certainty. When very low proportions of gas are to be tested for the size of the hydrogen flame may be increased with advantage, as is described below; but no observer could fail to see the smallest cap mentioned above with the 10 m.m. flame.

The advantage of increasing the size of the hydrogen flame when small percentages of gas are being looked for is shown by the results of the following experiments made by exposing the hydrogen safety-lamp in air containing 1 per cent and 0.5 per cent of coal-gas respectively: the height of the cap being noted in each mixture when the hydrogen flame was first 10 m.m., and then 15 m.m. in height.

Per cent.	M.m. cap.	M.m. cap.
1 gas ..	27 (flame 10 m.m.)	50 (flame 15 m.m.)
½ " ..	23 " "	38 " "

Attention is directed in the above statement to the height of the cap alone, but as a matter of fact, its change in general appearance is also very noticeable as the proportion of gas is increased. Very careful observation of the hydrogen flame in air free from gas serves to detect a slender and very pale cap. When the gas in the air reaches 0.25 per cent the cap becomes broader and pale grey in colour, but is still indefinite in outline, especially at its summit, and is seen only above the hydrogen flame. As the proportion of gas increases the flame becomes strikingly sharp and pointed in outline, distinctly bluish-grey in colour, and gradually broadens and extends down the sides of the hydrogen flame, finally enclosing it altogether and encircling the jet. At the same time, the hydrogen flame itself is constantly growing in every dimension, gaining in luminosity and acquiring a rose-red tip. It is well to have watched the above changes in the test-chamber, and to have become familiar with the appearance of the hydrogen flame in different percentages of gas before the flame is used for gas-testing.

The use of the hydrogen flame for gas-testing has the advantage of rendering possible the employment of a non-luminous flame, which can be immediately adjusted to any convenient size; not only may the size of the cap be thus increased at will by enlarging the flame, but it is possible to avoid the risk of losing the flame in the lamp, which is incurred by drawing down the wick very low when an oil flame is made use of for gas-testing.

The Solution of Antimony Chloride in Saturated Solutions of Sodium Chloride.—Antimony chloride, SbCl_3 , in contact with water, undergoes a partial decomposition which transforms it into oxichloride, SbOCl ,—a decomposition which obeys the general laws formulated by H. Sainte-Claire Deville. Without changing the reaction set up by the water, without modifying any of the general data which allow it to be classed among phenomena of dissociation, it is possible to displace the part of the acid, substituting for it a salt such as sodium chloride, and to obtain a solution of antimony perfectly neutral.—*Bull. Soc. Chim. de Paris*, No. 2, 1892.

ON THE
OCCLUSION OF HYDROGEN BY LEAD.

By JOHN SHIELDS, Ph.D., B.Sc.

SINCE the introduction of secondary batteries by Planté and Faure, a large amount of work has been done by various observers in order to obtain a clearer insight into the various changes which occur during the charging and discharging of the cells. The question of the occlusion of hydrogen by metallic lead, which has often been asked, has also received a good deal of attention, but the answers furnished by the different observers unfortunately do not agree. It is the object of this paper to bring together the evidence for and against the occlusion of hydrogen by lead, and to supplement it by some additional experiments.

Frankland (*Proc. Roy. Soc.*, xxxv., p. 67) was perhaps the first to institute experiments to decide this question. He proceeded by reducing red lead electrolytically, and examining the spongy substance which was thus obtained, in order to see whether it consisted solely of metallic lead or contained hydrogen associated with it in any way. The reduced mass was placed in a combustion tube and heated until the lead melted, but no measurable quantity of hydrogen was given off.

Graham found that palladium, which had served as the negative electrode during the electrolysis of dilute sulphuric acid, and which thereby becomes charged with a large quantity of hydrogen, possesses the property of reducing potassium ferricyanide to potassium ferrocyanide, potassium chlorate to potassium chloride, &c. Gladstone and Tribe ("The Chemistry of Secondary Batteries," p. 48), have applied this method to the spongy lead, and as the result of several experiments they found that the amount of hydrogen associated with the reduced lead was almost inappreciable.

Several authors have simply assumed, with no experimental evidence whatever, that hydrogen is occluded by spongy lead. The same assumption has also been made by Drzewiecki and Streintz, but these gentlemen have adduced facts which were believed to justify it. Drzewiecki (*La Lumière Electrique*, xxxv., 290) measured the potential difference between the two poles of his secondary battery and found it to be 2.15 volts. He then measured the difference of potential between each of the poles and a piece of clean lead which he immersed in the electrolyte, and obtained 0.2 and 1.7 volt respectively. From these observations Drzewiecki concludes that the difference in behaviour of plain and reduced lead is due to the absorption of hydrogen by the latter. That a difference does exist cannot be doubted, but it by no means follows that this is due to occluded hydrogen, especially as no other facts have been brought to light which justify this conclusion, whilst a great many tend to prove the reverse.

Streintz (*Wied. Ann.*, xxxviii., 355) has also described an experiment which was supposed to prove the occlusion of hydrogen by reduced lead. If a completely charged cell is disconnected from the charging current and closely observed, one can see bubbles of gas rising from both plates. The gas which is given off at first from the peroxide plate soon ceases; according to Gladstone and Tribe it is oxygen, probably produced by the action of peroxide of hydrogen on the peroxide of lead. The evolution of gas from the lead plate, however, continues for weeks and even months; it has been shown to be hydrogen, and in its production Streintz finds an argument for the hypothesis that it is occluded by the lead and afterwards slowly given off. The other possibility, namely, that it is produced by the action of the dilute sulphuric acid on the spongy lead, he rejects, as he says he would have been able to detect white sulphate of lead by means of the eye had any been formed. Now Thomson (*Thermochem. Untersuchungen*, iii., 335) has shown that lead belongs to that class of metals which decomposes water, and Gladstone and Hibbert (*Phil. Mag.*, August, 1890, and

January, 1891), have performed an experiment similar to that described by Streintz, but not content with the look of the plate they analysed it afterwards and found it to contain about 85 per cent of sulphate of lead; moreover, the sulphate of lead formed in secondary batteries, as Frankland has pointed out, is not perfectly white in colour. So that the hydrogen which is given off from the reduced lead is without doubt one of the products of the action of lead on dilute sulphuric acid, lead sulphate being formed at the same time.

This view has also been confirmed by Cantor (*Monats. fur Chemie*, xi., 444), who found that the amount of hydrogen which was disengaged was exactly equivalent to the sulphuric acid which was "fixed" during the disengagement. By means of a weighed cell in which the peroxide plate was replaced by a platinum electrode, he also succeeded in showing that no hydrogen was occluded by the lead. He estimated the total amount of hydrogen contained in the cell before charging and compared it with what was given off in the gaseous state during charging together with what remained behind in the electrolyte, and found that the two amounts agreed within the range of experimental error, which proves that no hydrogen could have entered into association with the lead electrode.

Thoma (*Zeit. fur Phys. Chem.*, iii., 91), has shown that iron wire occludes ten times its volume of hydrogen at the ordinary temperature, and according to the experiments of Bellati and Lussana (*Atti. R. Ist. Ven.*, i., Series VII., p. 1173), hydrogen diffuses through an iron plate which is used as the negative electrode on electrolyzing dilute sulphuric acid. Before applying this method to lead it was thought advisable to repeat some of the experiments of the Italian physicists, and so obtain confirmation of this very remarkable fact. A strong glass funnel with a stem about a metre long was therefore taken and a side tube fused on near the top. A piece of clean sheet iron such as is used in making telephones was supported on a porcelain filter plate and made to close the funnel air-tight by means of sealing-wax run in round its edges. The tube was then dipped into a trough of mercury alongside of another barometer, and after the air had been pumped out, the side tube was sealed up. We had thus two barometers, one of which was closed at the top by means of an iron plate, standing side by side, so that differences of level could easily be measured. After it was quite certain that the iron plate was sealed on perfectly air-tight, the funnel was filled with very dilute sulphuric acid, and the iron plate connected with the negative pole of a battery; a coil of platinum wire suspended in the acid served as the positive electrode. A few minutes after the circuit was completed the column of mercury began to descend. The following table, in which column I. gives the time in minutes, and column II. the depression in millimetres, will give some idea of the rate at which the hydrogen diffuses through the iron.

I.	II.	I.	II.
Min.	M.m.	Min.	M.m.
0	0	105	16.0
10	1.3	133	20.8
20	2.0	160	25.4
25	3.7	228	36.7
30	4.5	307	48.5
40	6.0	375	60.1
57	8.8	520	80.5
71	10.9	1360	169.5
87	13.4	1745	196.5

Bellati and Lussana have shown that the vacuum on the lower side of the iron plate is not the cause of the passage of the hydrogen through it, and that it merely magnifies the volume of the hydrogen and makes the diffusion more easily visible. With a modified form of a apparatus they have succeeded in obtaining pressures up to several atmospheres.

	Pt.		Pd.		Fe.		Cu.		Au.		Ag.	
	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	P.c.
Initial P.D.	1.20		1.014		0.164		0.712		1.096		0.959	
P.D. after polar., 0 min.	0.438		0.189		0.260		0.164		0.425		-0.243	
1 "	0.891	59.5	0.685	60.2	0.233	27.2	0.710	99.8	0.942	72.0	+0.781	84.8
2 "	0.945	66.2	0.726	65.0					1.000	85.6	0.850	90.5
3 "	0.979	71.0	0.740	67.0					1.028	89.9	0.864	91.8
4 "	0.986	71.8	0.740	67.0					1.041	91.6	0.891	95.9
5 "	0.997	73.1	0.750	68.1	0.225	36.5			1.055	93.8	0.918	96.8
10 "	1.003	74.0	0.754	68.6	0.222	39.6	0.712	100.0	1.090	99.0	0.946	98.6
30 "	1.025	77.0	0.781	71.8	0.214	47.9	0.712	100.0	1.096	100.0	0.959	100.0

	Pb.		Sn.		Zn.		Al.		Ni.		Carbon.	
	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	Per cent.	Volt.	P.c.
Initial P.D.	+0.178		0.231		-0.397		0.069		0.685		1.233	
P.D. after polar., 0 min.	-0.329		-0.341		-0.413		-0.329		0.301		-0.027	
1 "	+0.110	85.0	-0.041	52.5	-0.397	100.0	-0.055	69	0.658	96.0	+0.864	71.0
2 "	0.178	100.0	+0.014	57.2			+0.123	113	0.740	114.0	1.028	83.6
3 "			0.096	76.3			0.178	127	0.740	114.0	1.082	88.2
4 "			0.203	95.1			0.178	127				
5 "			0.223	98.6			0.164	124	0.726	110.8	1.096	89.2
10 "	0.178	100.0	0.223	98.6			0.137	117			1.123	92.2
30 "	0.178	100.0	0.223	98.6	-0.397	100.0			0.713	107.0	1.200	97.8

Having verified the experiments of Bellati and Lussana we substituted a thin lead plate for the iron one, but no depression of the mercury took place. This is exactly what we should expect of a metal which does not occlude hydrogen, were it not for the very remarkable fact that neither platinum nor palladium, both of which are known to occlude gases, permit of the passage of hydrogen through them under the same circumstances. Experiments with plates of these two metals carried out in precisely the same way, although allowed to go on for fourteen days in order that they might become fully saturated with hydrogen, showed no depression of the mercury.

On applying the method which Helmholtz and Root (*Monatsber. d. Berl. Acad. d. Wiss.*, 1876, p. 217) employed to show the occlusion of hydrogen by platinum to lead, a negative result was also obtained.

The rate at which the potential difference between a polarised plate and a non-polarisable electrode falls off, affords another method for investigating whether a given metal occludes hydrogen or not. The metal to be examined was dipped into a vessel of water to which a few drops of sulphuric acid had been added, and the potential difference between it and amalgamated zinc in a solution of zinc sulphate measured. It was found that this measurement could not in general be made at once, as differences amounting to several hundredths of a volt were frequently observed; after the lapse of about twenty or thirty minutes, however, the readings remained constant. A platinum plate acting as an anode was then placed in the liquid, and the metal under examination polarised for an hour,—in some cases for three or four hours,—and the current interrupted. Measurements of the potential difference between the various metals examined and zinc in a solution of zinc sulphate, were made at the moment of breaking the battery circuit, and afterwards at frequent intervals with Prof. Ostwald's modification of the capillary electrometer and a suitable compensating apparatus. The following table shows some of the results which were obtained. The first column gives the potential differences, and the second the percentage fall of the polarisation.

A cursory examination of the table enables one to see that the substances examined may be divided into two main groups: first, that in which the potential difference falls off very slowly; and second, that in which the original potential difference is regained after a few minutes; and these two groups, leaving carbon out of account, contain respectively the metals which do, and those which do not, occlude hydrogen. When hydrogen

occurs only superficially on a metal it quickly becomes oxidised, and the difference of potential due to it rapidly disappears; but when the hydrogen has entered into association with the metal, this process of oxidation occupies a much longer time, owing probably to diffusion, and consequently the original potential difference is regained only after the lapse of several hours.* Nickel and aluminium show the anomalous behaviour which has often been noticed by other observers; it is highly probable that neither of them was pure. In the case of zinc almost no polarisation effect was obtained. This agrees with the fact that very nearly the same electromotive force is required in order to separate zinc and hydrogen from their compounds, as Le Blanc (*Zeitsch. fur Phys. Chem.*, v., 467; viii., 299) has shown.

In conclusion, it is evident from the above table that lead belongs to that group of metals which does not occlude hydrogen, and as all the other evidence is in agreement with this fact, we are compelled to reject the hypothesis, which is sometimes advanced and which has recently been defended by Streintz and others, that hydrogen is occluded by lead and plays an important part in the chemistry of secondary batteries.

It is my pleasant duty to thank Prof. Ostwald for his kindness and help during this investigation.

Leipzig, December, 1891.

POSTSCRIPT.

Since the above was written another paper by Neumann and Streintz has appeared in the *Monatshefte fur Chemie*, xii., 642, the object of which is to prove the assumption which was made in a former paper, viz., that hydrogen is absorbed in large quantities by lead. Now the evidence which has just been shortly reviewed tends to prove the reverse of this; at the same time it ought to be carefully borne in mind that no attempt has been made to show that *absolutely no hydrogen* is absorbed by lead, for it is a well known fact that almost all substances possess the property of condensing gases and vapours on their surface. All that is maintained is, that lead practically occludes no hydrogen, and that it does not play the important part in the chemistry of secondary batteries which has often been ascribed to it.

In order to form an idea of the quantity of hydrogen which they assumed to be absorbed we may return to their experiment which has already been described and

* The table also indicates the percentage amount by which the potential difference, after various intervals, has approached the initial value.

criticised. They found that in about a week the spongy, lead gave off *forty-nine* times its volume of hydrogen gas and then it is stated that the spongy metal possesses not only the property of absorbing the gas, but also of giving it off again *in part*, so that *forty-nine* does not represent the total number of volumes absorbed.

Two different methods were employed. The first of these was simply a modification of Frankland's, and the result was practically identical with that which he obtained, although great precautions were taken to prevent the charged lead from coming into contact with the air, as thereby a portion of the absorbed hydrogen might be oxidised.

In the second method pure dry hydrogen (dried by means of phosphorus pentoxide), was led through melted lead contained in a U-tube. After the gas had passed through for 6 to 8 hours, the lead was allowed to cool down nearly to its melting-point, and the excess of hydrogen in the apparatus replaced by pure dry nitrogen. The U-tube was then connected with a combustion-tube containing ignited copper oxide, the other end of which had chloride of calcium tubes attached to it for the purpose of collecting water. In an experiment of this kind, however, where at the best only excessively small quantities of water were formed, the chloride of calcium ought to have been replaced by phosphorus pentoxide, as the nitrogen and oxygen which were employed were dried with this substance, and it is a well-known fact that gases so dried can take up water from chloride of calcium, which almost always contains a certain amount of moisture. After the apparatus was properly arranged and tested, oxygen was passed through it and the lead heated again to a higher temperature. Had any hydrogen been occluded by the lead it would have been converted into water and collected in the chloride of calcium tubes, but practically none was obtained. Another experiment was therefore made, but with this difference, that the melted lead was allowed to solidify completely before the excess of hydrogen was swept out by the nitrogen. The authors found that—

Grm. Water.	Grms. Lead.
I. 0.0022 was obtained when 200 were employed.	
II. 0.0003 " " " "	39.94 " "

It is perfectly evident from these numbers that the quantity of water obtained is far too small to form the basis of any conclusions as to the occlusion of hydrogen by lead, but Neumann and Streintz calculate from them that lead absorbs 0.15 and 0.11 times its volume of hydrogen respectively. Rather more than one-tenth of its volume forms a striking contrast with the numbers given in the former paper, and it appears to us that, instead of proving that lead absorbs large quantities of hydrogen, it shows that it absorbs very little or none at all. The quantity of water obtained in these experiments, too, is apt to be very considerably increased if the solidified lead mechanically encloses bubbles of hydrogen. But the reasoning adopted by Neumann and Streintz is as follows. It has been shown by Graham that palladium used as the cathode on electrolysing dilute sulphuric acid absorbs much more hydrogen than when simply heated in an atmosphere of that gas, and similarly, if it can be shown that melted lead absorbs a certain amount of hydrogen, then they consider themselves justified in assuming that lead, used as an electrode, will absorb very much more. It is needless to say, however, that this reasoning, which may or may not be perfectly correct, cannot be adduced as a proof of the assumption which was made in their former paper.

Leipzig, February 22, 1892.

ON THE ASSAY OF ORES OF ANTIMONY.

By AD. CARNOT.

As antimony has recently met with novel applications, the working of its ores has become much more active than heretofore. It has been complained, not without cause, that the assay of its ores by the usual processes of the dry way gave results very inaccurate and fluctuating in the hands of different operators. I have ascertained that the losses, always exceeding 8 per cent rise frequently up to 20 and even beyond 30 per cent of the true quantity, especially in poor ores.

After having made some attempts to diminish the losses by the dry process, which are always considerable on account of the volatility of antimony, I have studied a different method, the results of which have been much more satisfactory, and which on this account it seemed useful to make known.

The method consists, in principle, in dissolving the antimony in hydrochloric acid, in precipitating it with tin and weighing it in the metallic state. I indicate the precautions to be taken for sulphuretted ores, for oxides, and for those containing iron or lead.

1. *Sulphuretted Ores.*—We take from 2 to 5 grms. of the ore, according to its supposed percentage, so that we may operate upon about 1 gm. of metallic antimony. We attack it in a small flask with from 50 to 60 c.c. of concentrated hydrochloric acid, heating in the sand-bath, but not up to ebullition, so as to avoid losses by projection.

When the action seems to make no further progress we decant the clear liquid through a filter, adding in its stead a new quantity of acid, and resume the heating in the same manner until the sulphide is entirely dissolved. The acid is renewed once again, adding 1 or 2 drops of nitric acid to complete the attack, heating to *roo°*, and then washing the insoluble gangue with acid diluted with water.

The liquids decanted through the same filter are mixed with an equal volume of water; a blade of tin is introduced and heated to *80°* or *90°*. The precipitation begins at once, and for 1 gm. of antimony it is completed at the end of about 90 minutes.

The precipitate is washed by decantation, replacing the liquid by dilute hydrochloric acid to remove salts of tin and others derived from the attack and the precipitation. The metal is brought upon a tared filter, washed for some moments with hot water, and lastly with a little alcohol. The metallic antimony is then dried at *100°* and weighed upon the same filter. If the operation is thus conducted there is neither loss nor appreciable oxidation.

The percentage of antimony is thus determined accurately in a short time. In several experiments made with stibine mixed with quartz I found that the variations were ordinarily quite minimal, and at the most did not exceed 1 centigram,—that is 1-100th of the true percentage of the ores operated upon.

2. *Oxidised Ores.*—The oxides of antimony, often mixed with sulphides not as yet perfectly transformed by atmospheric agents, are sometimes attacked with great difficulty by concentrated hydrochloric acid. We are then exposed either to notable losses by volatilisation or to an incomplete solution of the antimony.

I thought that we might easily convert the oxides into attackable sulphides by heating them very gently in an atmosphere of hydrogen sulphide, according to the method which I formerly proposed for the production of metallic sulphides (*Comptes Rendus*, 1879, July 21).

The ore, in very fine powder, is put into a small flat-bottomed flask, in which the quantity of from 2 to 5 grms. forms a light layer permeable to gases. We cause an elbowed tube to descend almost down to the level of the ore, securing it in its place by means of a cork resting in

The Volatility of Urea and its Crystallisation by Means of Sublimation in a Vacuum.—Leon Bourgeois.—The sublimation of urea begins at about *120°* to *130°*, and it deposits crystals on the cold parts of the containing vessel.—*Bull. Soc. Chim. de Paris*, No. 2, 1892.

the neck of the flask. Through this tube there is passed a current of dry sulphuretted hydrogen. The flask is placed upon wire gauze at the height of 4 or 5 c.m. above the flame of a Bunsen burner with its rose so that the temperature may not exceed 300° , not producing any volatilisation of the antimony sulphide. The ore remains pulverulent, and is pervaded with hydrogen sulphide, which acts at once as a reducing agent and as a sulphuriser. The surface is renewed from time to time by shaking the flask. There is produced a little vapour of water and sulphur, which condense on the upper part of the sides. The conversion is complete in an hour. When cold the sulphide is attacked with concentrated hydrochloric acid in the same flask. The precipitation and weighing are then effected as in the former case.

Experience shows that the quantity of antimony remaining undissolved is quite insignificant.

Ores containing Iron or Lead.

It often happens that antimony ores contain iron, not only in the state of oxide or of pyrites, but also as ferrous sulphide combined with antimony sulphide, and soluble together in hydrochloric acid. Its presence, even in important quantity, does not interfere with or complicate the process. The presence of zinc, which is very rare in these ores, occasions no difficulty.

Lead, as sulphide or as oxide, is found in some varieties of antimony ores. It dissolves in hot concentrated hydrochloric acid; its chloride may partly crystallise out during the cooling of the liquid, but another portion is deposited on the sheet of tin and renders the weight of the antimony excessive.

We may easily detect the presence of lead in the precipitate, and even determine its quantity by converting it into sulphide by means of a solution of yellow sodium sulphide (prepared by boiling the monosulphide with flowers of sulphur). If we heat the metallic powder to 50° or 60° in the solution of polysulphide, the antimony is rapidly dissolved, and the residue of lead sulphide is washed, dried, and weighed. Eight-tenths of the weight of this sulphide represents the corresponding weight of the metallic lead, but as the lead generally undergoes oxidation during drying the quantity may be estimated practically at nine-tenths the weight of the lead sulphide. This is then the correction to be made.—*Comptes Rendus*, cxiv., p. 587.

THE DETERMINATION OF FLUORINE.

By AD. CARNOT.

FLUORINE enters into the composition of many natural substances, but we have often restricted ourselves to establishing its presence by qualitative experiments on account of the difficulties presented by its exact determination, especially in presence of silicates.

Many methods of determination have certainly been given by eminent analysts—Berzelius, H. Rose, Woehler, Fresenius; but in these methods accuracy has been obtained only by means of great complications or very minute precautions.

The method which I now propose, and which I have already applied to the analysis of a certain number of fluorine compounds capable of being attacked by concentrated sulphuric acid, has the advantage of being of easy execution, and of not being interfered with by the presence of carbonates or of organic substances; it can serve to show not merely the proportion of fluorine, but also that of silicon with satisfactory accuracy.

The process is founded, like several methods already known, on the disengagement of fluorine in the state of gaseous silicon fluoride; its novelty consists in the method of determining the volatile compound. In place of calculating it by the difference of two weighings Woehler, Fresenius), or according to the weight of the

calcium fluoride obtained after a tedious separation of the silica (Berzelius, H. Rose, and recently H. Lasne). I receive the silicon fluoride in a rather concentrated solution of pure potassium fluoride, with which it forms a precipitate of potassium silicofluoride, the weight of which enables us to calculate the fluorine, and if needful, the silicon, $\text{SiF}_2 + \text{KF} = \text{KF.SiF}_2$, or $\text{F}_4 + 2\text{KF} = \text{K}_2\text{F}_6$.

I indicate briefly the arrangement of the apparatus and the course of the operation.

The mixture of fluoride and silicate is acted upon by concentrated sulphuric acid in a small flask holding 150 c.c., to the bottom of which there is conveyed a slow current of air, or of carbonic acid, which has been perfectly dried by passing through bottles filled with sulphuric acid. The gaseous current is then conveyed by an elbow-tube to the bottom of a flask containing a little mercury and above it 20 c.c. of a solution of pure potassium fluoride (1 part in 10). Beyond this there is an aspirator arranged so as to regulate the current.

The extremity of the tube which enters the flask should be drawn out to a point and bent back, opening 2 or 3 m.m. below the surface of the mercury, so that it is not moistened by the aqueous solution.

The flask and the tube must have been perfectly dried either in the stove or after the apparatus has been connected by the action of the dry gas conjointly with that of heat, so as to avoid any decomposition of silicon fluoride by moisture. The elbow-tube carries an empty bulb intended to retain the traces of sulphuric acid which may be carried along by the current of gas. There must be added a tube filled with pumice saturated with dehydrated copper sulphate to arrest the vapours of hydrochloric acid, when the fluorine substance contains also chlorides (apatite, &c.), for these vapours reacting upon the potassium fluoride might liberate hydrofluoric acid, which would attack the sides of the flask and the surface of the mercury.

The quantity of material taken for analysis should be such that the quantity of fluorine does not exceed about 0.100 grm.; we take therefore 0.200 grm. of rich fluorides (fluor-spar, cryolite, &c.), and up to 2 grms. or upwards of substances poor in fluorine (natural phosphates, bones, &c.). We mix the substance intimately in an agate mortar with ignited quartz in very fine powder in such proportions that there may be at least 10 parts of silica to 1 part of fluorine. The quantity of silica must be still greater if the matter under examination contains less than 5 or 6 per cent of fluorine.

When the apparatus has been fitted up, tested by means of the aspirator, and well dried, the current of gas is stopped for a few moments, we introduce into the flask the mixture to be attacked, and pour in 40 c.c. of pure concentrated sulphuric acid; then the current of gas is allowed to resume and the flask is heated upon a plate of iron, under which a gas-burner is lighted. At the same distance from the burner we place a similar flask also containing 40 c.c. of sulphuric acid, into which plunges a thermometer which indicates in a sufficiently approximate manner the temperature at which the action takes place (Fresenius); we regulate the burner so as to reach a temperature close upon 160° , which must never be exceeded.

The small flask is shaken from time to time so as to liberate the bubbles of gas which form in the liquid or against the sides; they generally cease to be formed after 1½ or 2 hours, and we may soon after consider the attack as completed.

The potassium fluoride contains then a gelatinous precipitate of silicofluoride which is scarcely visible, and which would soon settle if the liquid were left in repose; but without waiting for this we detach the tubes which lead to the flask, decant the aqueous solution, wash the mercury and the flask with several successive portions of water, and collect the liquids, the total volume of which should not exceed 100 c.c.; we add an equal volume of alcohol of the strength of 90 per cent, we mix the whole, and allow it to deposit.

When the precipitate is properly collected together after having decanted off the supernatant liquid and replaced it with dilute alcohol, we collect the deposit upon a tared filter, and finish the washing with alcohol diluted with its own volume of water, making use of the filter pump until the liquid no longer occasions any turbidity in a solution of barium chloride. We dry at 100° until the weight is constant, and calculate the fluorine of the silicon fluoride. For $\text{KF} \cdot \text{SiF}_2$ we have $F_2 = 0.3451$.

For the accuracy of the determination it is essential that the reagents employed should be free from fluorine. This is certainly the case with sulphuric acid if it has been heated to close upon its boiling-point. It is the same with ignited quartz. However, both may be tested once for all in a blank experiment. The potassium fluoride should be free from silicofluoride; it is necessary to ascertain this point by dissolving 2 grms. of the salt in 100 c.c. of water, and adding an equal volume of alcohol at 90 per cent. No deposit should be produced even if the liquid is allowed to remain at rest for 24 hours.

In the analysis of a fluorine silicate one and the same operation may serve for the determination of the fluorine and of the silicon, provided that the sides of the flask are not sensibly attacked. This result is obtained either when we operate upon a silicate poor in fluorine, or if we mix very intimately by trituration in an agate mortar the fluorine substance with a great excess of quartz finely levigated and of pure silica, which is ignited and weighed exactly. The silicon is then calculated in two portions. A small portion is found along with the fluorine in the precipitate of silicofluoride. For $\text{KF} \cdot \text{SF}_2$ we have $\text{Si} = 0.12714$; $\text{SiO}_2 = 0.28154$.

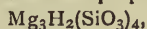
The other portion is found in the state of silica in the residue of the action of sulphuric acid, and may be separated and determined by the ordinary methods. The weight of the silica added must of course be deducted from the weight obtained.—*Comptes Rendus*, cxiv., p. 750.

THE FRACTIONAL ANALYSIS OF SILICATES.*

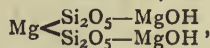
By F. W. CLARKE.

(Concluded from p. 189).

In the case of talc, $\text{Mg}_3\text{H}_2\text{Si}_4\text{O}_{12}$, the foregoing principle finds ready application. For this mineral two constitutional formulæ have been proposed; one,—

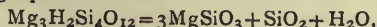


regards it as an acid metasilicate; the other,—

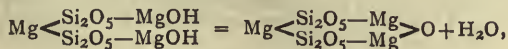


represents it as a basic salt of the acid $\text{H}_2\text{Si}_2\text{O}_5$. Now talc is practically unattacked by hydrochloric acid either wet or dry, and so a presumption is established in favour of the metasilicate formula. The group $\text{Mg}-\text{OH}$ is apparently not present. This view, fortunately, is maintained by other evidence, which also serves to illustrate another principle in fractional analysis.

When talc is sharply and quickly ignited, so as to produce complete dehydration, silica is set free. That silica may then be dissolved out by boiling with an aqueous solution of sodium carbonate, and estimated. One-fourth of the total silica of the mineral was thus liberated, its quantitative determination varying only 0.21 per cent from the exact amount required. This decomposition represents a splitting up of talc in accordance with the following equation:—



which is reconcilable only with the metasilicate formula. If the pyrosilicate formula were correct, the expulsion of water would be indicated thus:—



* *Journal of the American Chemical Society*, xiii., No. 10.

and it is not easy to see how silica could be split off. In short, the separation of the silica into two fractions, and the evidence furnished by the stability of the talc towards acids, prove that the hydrogen of the mineral is acid hydrogen, and establish the constitution of the species. Of all the possible formulæ for talc, the metasilicate formula alone satisfies the experimental conditions.

It has already been stated that the silicates under discussion, with the exception of talc, are readily decomposable by aqueous hydrochloric acid. Upon ignition, however, most of them split up into soluble and insoluble portions, which can be separately investigated. Serpentine, for example, splits up into soluble olivine and insoluble enstatite, water, of course, being eliminated. This particular case of decomposition by heat has long been known, but among the chlorites and the clintonite micas are found some new applications of the principle. Four examples, closely related, may be cited here, namely, three chlorites of similar type, and xanthophyllite, variety walnewite, from Siberia.

The method of investigation was as follows:—Each mineral, of which a sample had been previously analysed, was strongly ignited in powder over a blast. The operation was performed in a covered platinum crucible, and the ignition lasted for several hours. The material was next digested with strong hydrochloric acid, the mixture was evaporated to dryness, the residue treated with weak acid, and finally filtered off. There remained in the filter, of course, the insoluble portions of the minerals, plus the silica which had been liberated from the soluble parts. This silica was then removed by boiling with sodium carbonate solution, and the undissolved remainder was washed, weighed, and separately analysed. In each of the four cases it proved to have the composition of spinel, MgAl_2O_4 , and in quantity it bore a definite relation to the formulæ of the original minerals. The latter were as follows, with their empirical formulæ subjoined:—

- Ripidolite (elinochlore), from West Chester, Pa.
- Clinochlore, from Slatoust, Urals.
- Leuchtenbergite, from Slatoust, Urals.
- Walnewite, from near Slatoust.

- $\text{Al}_{38}\text{Mg}_{86}\text{H}_{140}(\text{SiO}_4)_{50}\text{O}_{113}$.
- $\text{Al}_{38}\text{Mg}_{87}\text{H}_{143}(\text{SiO}_4)_{52}\text{O}_{113}$.
- $\text{Al}_{42}\text{Mg}_{86}\text{H}_{143}(\text{SiO}_4)_{50}\text{O}_{121}$.
- $\text{Al}_{86}\text{Ca}_{24}\text{Mg}_{52}\text{H}_{50}(\text{SiO}_4)_{28}\text{O}_{174}$.

Upon dehydration these become:—

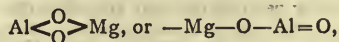
- $\text{Al}_{38}\text{Mg}_{86}(\text{SiO}_4)_{50}\text{O}_{43}$.
- $\text{Al}_{38}\text{Mg}_{87}(\text{SiO}_4)_{52}\text{O}_{42}$.
- $\text{Al}_{42}\text{Mg}_{86}(\text{SiO}_4)_{50}\text{O}_{49}$.
- $\text{Al}_{86}\text{Mg}_{52}\text{Ca}_{24}(\text{SiO}_4)_{28}\text{O}_{149}$.

Here we have throughout an excess of oxygen over the group SiO_4 , and to that excess the amount of spinel formed by ignition is almost quantitatively proportional.

That a decomposition of this sort furnishes strong evidence relative to the constitution of the minerals in question is clear without argument. Since, however, it is the purpose of the present paper merely to give a brief indication of methods in fractional analysis, an elaborate theoretical discussion would be out of place in it. The data, in all their relations, are being fully considered elsewhere (*Am. Journ. Sci.*, O&A, Nov., Dec., 1890; Sept., 1891; March, April, 1892), and only a short notice of their bearing is needed here. In the chlorites the group $\text{Mg}-\text{OH}$ is certainly present; and the three examples here given all reduce to the general formula $\text{Mg}_2(\text{SiO}_4)_2\text{R}'_4$, in which R' is partly H, partly MgOH , and partly AlO_2H_2 . The juxtaposition of the two latter groups serves to explain the formation of spinel upon ignition; while the soluble portions of the decomposed material appear to be mixtures of olivine and magnesian garnet, minerals which are common sources of chlorites in nature. Quite recently, Tschermak has sought to show that these particular chlorites are mixtures of amesite and serpentine. But serpentine, when ignited, yields insoluble enstatite,

while the three chlorites studied give only spinel in the residue undissolved by hydrochloric acid. The inference is that the chlorites contain no serpentine molecules, and Tschermak's view becomes untenable.

In the case of the walnewite, the spinel reaction has peculiar interest. In that mineral, the most basic known member of the clintonite group, there is good reason for assuming the existence of a univalent group—



each form of expression having its own theoretical advantages. The walnewite itself appears to be a mixture of isomorphous molecules, among which the compound $(\text{AlO}_2\text{Mg})_4\text{SiO}_4$ is predominant. Such a compound might easily split up into olivine and spinel, $\text{Mg}_2\text{SiO}_4 + 2\text{MgAl}_2\text{O}_4$, and the quantity of spinel actually formed when walnewite is decomposed by heat is almost exactly the amount required by theory. Two of the groups $-\text{AlO}_2\text{Mg}$, coalesce, with removal of one atom of magnesium, to form spinel, while the magnesium thus eliminated goes into the soluble olivine. The fact that the clintonite micas are almost invariably associated with spinel in nature, and frequently also with members of the olivine group, is very suggestive in this connection. The evidence of natural association and the evidence from the laboratory converge to one set of conclusions.

In the light of the foregoing statements the term "fractional analysis" practically defines itself. It is really an attempt at rational, as distinguished from empirical analysis; and it brings into the mineralogical laboratory the methods of the organic chemist. As yet, little more than a beginning has been made, but the field is promising and should yield a rich crop of valuable data. The researches are still in progress, and the results will be made public as rapidly as may be possible.

ON THE RELATIVE DENSITIES OF HYDROGEN AND OXYGEN. II.*

By Lord RAYLEIGH, Sec.R.S.

In a preliminary notice upon this subject (*Roy. Soc. Proc.*, vol. xliii., p. 356, Feb., 1888), I explained the procedure by which I found as the ratio of densities 15.884. The hydrogen was prepared from zinc and sulphuric, or from zinc and hydrochloric, acid, and was liberated upon a platinum plate, the generator being, in fact, a Smee cell, enclosed in a vessel capable of sustaining a vacuum, and set in action by closing the electric circuit at an external contact. The hydrogen thus prepared was purified by corrosive sublimate and potash, and desiccated by passage through a long tube packed with phosphoric anhydride. The oxygen was from chlorate of potash, or from mixed chlorates of potash and soda.

In a subsequent paper on the "Composition of Water" (*Roy. Soc. Proc.*, vol. xlv., p. 425, Feb., 1889), I attacked the problem by a direct synthesis of water from weighed quantities of the two component gases. The ratio of atomic weights thus obtained was 15.89.

At the time when these researches were commenced, the latest work bearing upon the subject dated from 1845, and the number then accepted was 15.96. There was, however, nothing to show that the true ratio really deviated from the 16:1 of Prout's law, and the main object of my work was to ascertain whether or not such deviation existed. About the year 1888, however, a revival of interest in this question manifested itself, especially in the United States, and several results of importance have been published. Thus Professor Cooke and Mr. T. W. Richards found a number which, when

corrected for an error of weighing that had at first been overlooked, became 15.869.

The substantial agreement of this number with those obtained by myself seemed at first to settle the question, but almost immediately afterwards there appeared an account of a research by Mr. Keiser, who used a method presenting some excellent features, and whose result was as high as 15.949. The discrepancy has not been fully explained, but subsequent numbers agree more nearly with the lower value. Thus Noyes obtains 15.896, and Dittmar and Henderson give 15.866.

I had intended further to elaborate and extend my observations on the synthesis of water from weighed quantities of oxygen and hydrogen, but the publication of Professor E. W. Morley's masterly researches upon the "Volumetric Composition of Water" (*Amer. Journ. Sci.*, March, 1891) led me to the conclusion that the best contribution that I could now make to the subject would be by the further determination of the relative densities of the two gases. The combination of this with the number 2.0002,* obtained by Morley as the mean of astonishingly concordant individual experiments, would give a better result for the atomic weights than any I could hope to obtain directly.

In all work of this sort the errors to be contended with may be classed as either systematic or casual. The latter are eliminated by repetition, and are usually of no importance in the final mean. It is systematic errors that are most to be dreaded. But although directly of but little account, casual errors greatly embarrass a research by rendering difficult and tedious the detection of systematic errors. Thus in the present case almost the only source of error that can prejudice the final result is impurity in the gases, especially in the hydrogen. The better the hydrogen, the lighter it will prove; but the discrimination is blunted by the inevitable errors of weighing. After perhaps a week's work it may become clear that the hydrogen is a little at fault, as happened in one case from penetration of nitrogen between the sealed-in platinum electrodes and the glass of the generator.

Another difficulty which affects the presentation of results turns upon the one-sided character of the errors most to be feared. As has been said, impure hydrogen can only be too heavy, and another important source of error, depending upon imperfect establishment of equilibrium of pressure between the contents of the globe and the external atmosphere, also works one-sidedly in the same direction. The latter source of error is most to be feared immediately after a re-greasing of the tap of the globe. The superfluous grease finds its way into the perforation of the plug, and partially blocks the passage, so that the six minutes usually allowed for the escape of the initial excess of pressure in the globe may become inadequate. Partly from this cause and partly from incomplete washing out of nitrogen from the generator, the first filling of a set was so often found abnormally heavy that it became a rule in all cases to reject it. From these and other causes, such as accidental leakages not discovered at the time, it was difficult to secure a set of determinations in which the mean really represented the most probable value. At the same time, any arbitrary rejection of individual results must be avoided as far as possible.

In the present work two objects have been especially kept in view. The first is simplicity upon the chemical side, and the second the use of materials in such a form that the elimination of impurities goes forward in the normal working of the process. When, as in the former determinations, the hydrogen is made from zinc, any im-

* It should not be overlooked that this number is difficult to reconcile with views generally held as to the applicability of Avogadro's law to very rare gases. From what we know of the behaviour of oxygen and hydrogen gases under compression, it seems improbable that volumes which are as 2.0002:1 under atmospheric conditions would remain as 2:1 upon indefinite expansion. According to the formula of Van der Waals, a greater change than this in the ratio of volumes is to be expected.

* From the *Proceedings of the Royal Society*, vol. 1. Read Feb. 18, 1892.

purity which that material may contain and communicate to the gas cannot be eliminated from the generator; for each experiment brings into play a fresh quantity of zinc, with its accompanying contamination. Moreover, the supply of acid that can be included in one charge of the generator is inadequate, and good results are only obtained as the charge is becoming exhausted. These difficulties are avoided when zinc is discarded. The only material consumed during the experiments is then the water, of which a large quantity can be included from the first. On the other hand, the hydrogen liberated is necessarily contaminated with oxygen, and this must be removed by copper contained in a red-hot tube. In the experiments to be described, the generator was charged with potash,* and the gases were liberated at platinum electrodes. In the case of a hydrogen filling the oxygen blew off on one side from a mercury seal, and on the other the hydrogen was conveyed through hot tubes containing copper. The bulk of the aqueous vapour was deposited in a small flask containing strong solution of potash, and the gas then passed over solid potash to a long tube packed with phosphoric anhydride. Of this only a very short length showed signs of being affected at the close of all operations.

With respect to impurities, other than oxygen and oxides of hydrogen, which may contaminate the gas, we

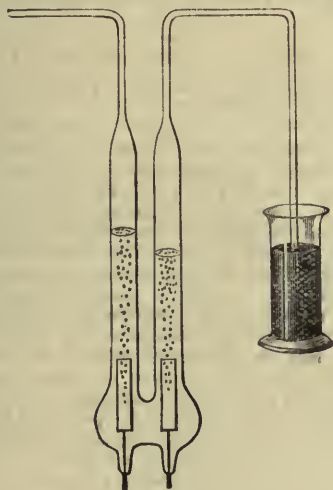


FIG. 1.

have the following alternative. Either the impurity is evolved much more rapidly than in proportion to the consumption of water in the generator, or it is not. If the rate of evolution of the impurity reckoned as a fraction of the quantity originally present, is not much more rapid than the correspondingly reckoned consumption of water, the presence of the impurity will be of little importance. If on the other hand, as is probable, the rate of evolution is much more rapid than the consumption of water, the impurity is soon eliminated from the residue, and the gas subsequently generated becomes practically pure. A similar argument holds good if the source of the impurity be in the copper, or even in the phosphoric anhydride; and it applies with increased force when at the close of one set of operations the generator is replenished by the mere addition of water. It is, however, here assumed that the apparatus itself is perfectly tight.

Except for the reversal of the electric current, the action of the apparatus is almost the same whether oxygen or

hydrogen is to be collected. In the latter case the copper in the hot tubes is in the reduced, and in the former case in the oxidised, state. For the sake of distinctness we will suppose that the globe is to be filled with hydrogen.

The generator itself (Fig. 1) is of the U-form, with unusually long branches, and it is supplied from Grove cells with about 3 amperes of electric current. Since on one side the oxygen blows off into the air, the pressure in the generator is always nearly atmospheric. Some trouble has been caused by leakage between the platinum electrodes and the glass. In the later experiments to be here recorded these joints were drowned with mercury. On leaving the generator the hydrogen traverses a red-hot tube of hard glass charged with copper,* then a flask containing a strong solution of potash, and afterwards a second similar hot tube. The additional tube was introduced with the idea that the action of the hot copper in promoting the union of the hydrogen with its oxygen contamination might be more complete after removal of the greater part of the oxygen, whether in the combined or in the uncombined state. From this point onward the gas was nearly dry. In the earlier experiments the junctions of the hard furnace tubes with the soft glass of the

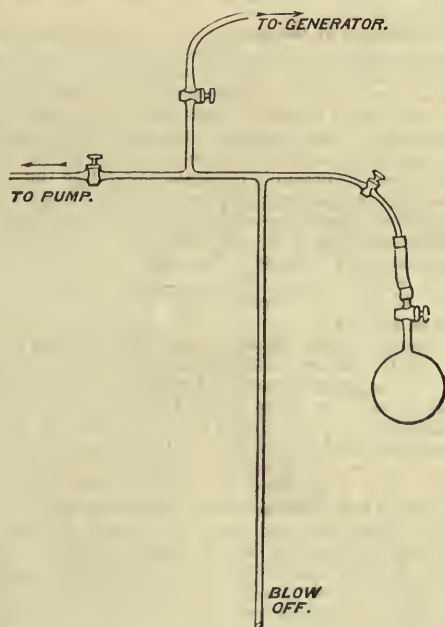


FIG. 2.

remainder of the apparatus were effected by fusion. One of these joints remained in use, but the others were replaced by indiarubber connections *drowned in mercury*. It is believed that no leakage occurred at these joints; but as an additional security a tap was provided between the generator and the furnace, and was kept closed whenever there was no forward current of hydrogen. In this way the liquid in the generator would be protected from any possible infiltration of nitrogen. Any that might find its way into the furnace tubes could easily be removed before the commencement of a filling.

Almost immediately upon leaving the furnace tubes the gas arrives at a tap which for distinctness may be called the regulator. In the generator and in the furnace tubes the pressure must be nearly atmospheric, but in the globe there is (at the commencement) a vacuum. The transition from the one pressure to the other takes place

* At the suggestion of Professor Morley, the solution was freed from carbonate or nearly so, by the use of baryta, of which it contained a slight excess.

* The copper must be free from sulphur; otherwise the contamination with sulphuretted hydrogen is somewhat persistent.

at the regulator, which must be so adjusted that the flow through it is approximately equal to the production of gas. At first the manipulation of the regulator was a source of trouble and required almost constant attention, but a very simple addition gave the desired control. This was merely a long wooden arm, attached to the plug, which served both as a lever and as an indicator. Underneath the pointed extremity was a small table to which its motions could be referred. During the first two-thirds of a filling very little re-adjustment was needed, and the apparatus could be left for half an hour with but little fear of displacing too much the liquid in the generator. Towards the close, as the motive force fell off, the tap required to be opened more widely. Sometimes the recovery of the level could be more conveniently effected by insertion of resistance into the electric circuit, or by interrupting it altogether for a few minutes. Into details of this kind it is hardly necessary to go further.

From the regulator the gas passed to the desiccating tubes. The first of these was charged with fragments of solid potash, and the second with a long length of phosphoric anhydride. Finally, a tube stuffed with glass wool intercepted any suspended matter that might have been carried forward.

The connexion of the globe with the generator, with the Töppler, and with the blow-off, is shown in the accompanying Fig. 2. On the morning of a projected filling the vacuous globe would be connected with the free end of the stout-walled india-rubber tube, and secured by binding wire. The generator being cut off, a high vacuum would be made up to the tap of the globe. After a couple of hours' standing the leakage through the india-rubber and at the joints could be measured. The amount of the leakage found in the first two hours was usually negligible, considered as an addition to a globeful of hydrogen, and the leakage that would occur in the hours following would (in the absence of accidents) be still smaller. If the tests were satisfactory, the filling would proceed as follows:—

The electric current through the generator being established and the furnace being heated, any oxygen that might have percolated into the drying tubes had first to be washed out. In order to do this more effectively a moderate vacuum (of pressure equal to about 1 inch of mercury), was maintained in the tubes, and up to the regulator by the action of the pump. In this way the current of gas is made very rapid, and the half hour allowed must have been more than sufficient for the purpose. The generator was then temporarily cut off, and a high vacuum produced in the globe connexion and in the blow-off tube, which, being out of the main current of gas, might be supposed to harbour impurities. After this the pump would be cut off, the connexion with the generator re-established, and finally, the tap of the globe cautiously opened.

The operation of filling usually occupied from two to three hours. When the gas began to blow off under an excess of pressure represented by about half an inch of mercury, the blow-off cistern was lowered so as to leave the extremity of the tube free. For two minutes the current of gas from the generator was allowed to flow through, after which the generator was cut off, and the globe left in simple communication with the atmosphere, until it was supposed that equilibrium of pressure had been sufficiently established. Doubts have at various times been felt as to the interval required for this purpose. If too little time is allowed, there will remain an excess of pressure in the globe, and the calculated weight of the filling will come out too high. On the other hand, an undue prolongation of the time might lead to a diffusion of air back into the globe. In a special experiment no abnormal weight was detected after half an hour's communication, so that the danger on this side appeared to be small. When the passages through the taps were free from grease, one or two minutes sufficed for the establishment of equilibrium, but there was always a possibility

of a partial obstruction. In the results to be presently given, four minutes were allowed after the separation from the generator. It may be remarked that a part of any minute error that may arise from this source will be eliminated in the comparison with oxygen, which was collected under like conditions.

The reading of the barometers and thermometers at the moment when the tap of the globe was turned off took place as described in the former paper. The arrangements for the weighings were also the same.

In the evacuations the process was always continued until, as tested by the gauge of the Töppler after at least a quarter of an hour's standing, the residue could be neglected. Here, again, any minute error would be eliminated in the comparison of the two gases.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, April 8th, 1892.

Dr. J. H. GLADSTONE, F.R.S., Past President, in the Chair.

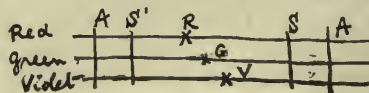
MR. C. S. MITCHELL was elected a member of the Society.

MR. WALTER BAILY, M.A., read a paper "*On the Construction of a Colour Map.*"

By the term "colour map," the author meant a diagram, each point of which defines by its position some particular colour. Captain Abney had shown that all colours except the purples could be formed by adding white light to some spectrum colour; whilst all except the greens could be made to produce white by the addition of some spectrum colour. There were therefore two ways in which colours, other than greens and purples, could be indicated. In one of these, the ordinate of a point might represent the spectrum colour by its wavelength and the abscissa, measured to the right of a vertical spectrum line, the amount of white light to be added to the spectrum colour to produce the colour represented by the point. In the other, the abscissa of a point situated on the left of the spectrum line represents the quantity of white light produced by the addition of the spectrum colour to the colour indicated by the point.

Regarding the spectrum colours as formed by mixing three primary colours (red, green, and violet) in varying proportions, three curves were drawn to the left of the spectrum line whose abscissæ represented respectively the proportions of the three primary colours present in the corresponding spectrum colour. Horizontal distances from any point to these curves show the proportions in which the primary colours are to be mixed to produce the particular colour defined by that point. For points between the curves, the horizontal distances are not measured all in one direction, and therefore indicate abnormal or imaginary colours.

The principle of the map was further illustrated by a sort of colour staff, consisting of three horizontal lines representing the three primary colour sensations (see Fig.)



of such luminosities that equal lengths of the three lines indicate white light. If points R, G, V, be taken in these lines, then a cross line, A, will cut off lengths A R, A G, A V, whose mixture will produce a certain colour. If, now, A be moved parallel to itself towards the right, the colour will change by the addition of white light; moving

A to the left means a subtraction of white light. When R, G, and V are properly chosen, a certain position, S, of the cross line corresponds to a spectrum colour. The whole of the series of colours which can be obtained by adding white light to that spectrum colour, can then be represented by sliding A towards the right. Positions S' and A' give colours complementary to S and A.

The distinguishing features of such a series of colours are the differences R-G and G-V, and the author calls the ratio $\frac{R-G}{G-V}$ the "colour index." Passing up the

spectrum from red to violet, the index, which is first large and positive, diminishes and becomes negative between the yellow and blue; it then passes through infinity and becomes positive and decreases to zero.

The subject of determining the indices of colours resulting from the mixture in various proportions of two other colours whose indices were known was considered, and diagrams showing the various curves exhibited. Experimental methods of determining the proportions of the primary colour sensations constituting the spectrum tints were described.

A VISITOR enquired how the author's system provided for the class of colours outside the red and violet. He also desired a definition of "white light." He himself had never been able to produce pure white by mixture of colours, for a reddish violet generally resulted. On the other hand, he found it possible to match any other colour by mixture.

Prof. CAREY FOSTER thought Helmholtz was the first to propound the laws which the author had attributed to Captain Abney. He wished to know how the amounts of colour sensation were supposed to be measured. White light he considered ought to be defined as light in which a normal eye, not fatigued, could perceive no preponderance of any colour.

Mr. BLAKESLEY said that if white light was a mixture and only two unknowns were necessary, then any colour could be produced by the mixture of two other colours.

Dr. SUMNER pointed out that white light was by no means a constant colour, but depended greatly on the source. He thought the author's map of a more absolute nature than that proposed by Maxwell.

Dr. HOFFERT enquired whether the intensities of each spectrum colour had been considered equal or otherwise taken into account, and also whether the results arrived at would be true for intensities other than those shown.

Mr. BAILY, in reply, said Captain Abney had found the light from the crater in the positive carbon of an electric arc to be the most constant white, and, in his method of experimenting, errors due to variation of the source cancel led. The quantity of any spectrum colour was defined by the breadth of the band used; the breadth being measured on the scale of wave-lengths.

A paper on "A Mnemonic Table for Changing from Electrostatic to Practical and C.G.S. Units" was read by Mr. W. GLEED, M.A.

In the table which is given below the abbreviations Stat. and Mag. are used to denote the electrostatic and electromagnetic units, and v stands for 3×10^{10} :—

To form the table, the numbers 9, 8, 1 in the middle of the second line give the value of "g." The end numbers are duplicated, giving 9, 9, 8, 1, 1. Below them, in the fourth line, come the names of the practical units, the initials forming the word "fovac." Remembering that the electromagnetic units of resistance and potential were too small for practical use, one places mag. above both ohm and volt. Ohm's law and definitions then show that

the practical units of capacity, current, and quantity must be less than the electromagnetic unit; hence, mag. must be written below farad, ampère, and coulomb, since the practical units are intermediate in magnitude between stat. and mag., the vacant spaces are then filled in by stat. The v 's in the bottom line are added in from memory. Several examples showing the use of the table are worked out in the paper accompanying the table.

A paper on "The Law of Colour in Relation to Chemical Constitution," by WILLIAM AKROYD, was read by Mr. BLAKESLEY.

The author has observed that in cases of compounds having a constant radical R and a variable radical R', the effect of an increase in the molecular weight of R' is to make the colour of the compound tend towards the red end of the colour scale. Exceptions are, however, noted.

Mr. H. M. ELDER questioned the author's conclusions, saying that in many cases the colours tend towards blue.

NOTICES OF BOOKS.

Saunders' Question Compounds, No. 23. *Essentials of Medical Electricity.* By D. D. STEWART, M.D., and E. S. LAWRENCE, M.D. Philadelphia: W. B. Saunders. 1892. Small 8vo., pp. 156.

WE cannot free ourselves from the suspicion that the work before us is what plain-spoken people do not scruple to call a "cram-book." But if so the information supplied should, at least, be accurate. Now, we read here (p. 25) that "metals are the best available conductors of electricity. Zinc, tin, and iron, named in their order of merit, head the list." If the authors had taken the trouble to consult some standard authority, e.g., Ganot's "Physics," latest edition, they would have found that if we take the conductivity of silver at 100.0, and that of copper at 99.9, zinc has only 29.0, iron 16.8, and tin 13.1, so that they are much nearer the bottom than the head of the list.

We can scarcely accept the statement that electricity exists in three forms: Galvanic, Faradic, and Franklinic, or static electricity. Surely static electricity had been known and experimented upon before the days of Franklin. This, in fact, the authors admit in speaking of the experiments of Dr. Gilbert.

We notice a few errors which with a little more care might have been avoided. Thus the name of the illustrious Danish *savant* Oersted is in one place written "Oerstead." Leclanché figures here as Le Clanche. The words "intrauterine" and "extrauterine"—the latter especially—would read better if dissociated.

As regards the use of electricity in the treatment of disease we are unable to say whether the directions here laid would meet with the approval of leading medical authorities. It is high time, however, that medical electricity should be taken out of the hands of the charlatans by whom it is now exploited with equal audacity and success, using the last word merely of course in a pecuniary point of view.

On the Composition of Pinnaglobine.—a Novel Globuline.—Dr. A. B. Griffiths.—The substance in question is obtained from the blood of *Pinna squamosa*. Its composition is $C_{724}H_{985}N_{182}MnS_4O_{210}$. It does not combine with NO_2 or CO .—*Comptes Rendus*, vol. cxiv., No. 14.

Units of—	Capacity.	Resistance.	Potential.	Current.	Quantity.
Powers of 10 for practical and magnetic units	9	9	8	1	1
Small unit	Stat.	Mag.	Mag.	Stat.	Stat.
Practical unit	Farad.	Ohm.	Volt.	Ampère	Coulomb.
Large unit	Mag.	Stat.	Stat.	Mag.	Mag.
Factor for stat. and mag.	v^2	v^2	v	v	v

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., No. 2.

Certain Organic Haloid Derivatives.—C. Chabrie. —The author concludes that for 4 chlorine atoms of CCl_4 we may substitute the residues of 4 mols. of monosodium malonic ether (deprived of their atom of sodium). A new octobasic acid has thus been obtained. If we try to substitute the 4 residues of 4 mols. of sodium phenate (deprived of their atom of sodium) for the 4 atoms of chlorine of CCl_4 we cannot succeed, on account of the departure of the chlorine into an intermediate molecule, —a process promoted by the alkalinity of the medium. A synthesis of aurine has been effected in this manner. If organic haloid compounds are treated with silver fluoride in a sealed tube we obtain the corresponding fluorides. Methylene fluoride is antiseptic and not irritating. It destroys the bacillus of tuberculosis and the urinary pyrogenous bacterium. $\text{C}_2\text{H}_4\text{F}_2$ does not possess these properties, and we have examined how the number of the atoms of fluorine and the arrangement of the atoms in the molecule cause their physiological action to vary. The fluorides obtained are in general saponifiable by alcoholic potassa. The saponification of ethylene fluoride in the cold by means of lime produces a synthesis of glycol. The author has lastly shown the reciprocal substitutions occurring between boron and carbon in the haloid compounds and the oxides.

Method of Preparing Carvacrol.—A. Reychler.

Certain Derivatives of Carvacrol.—A. Reychler.

Constitution of Carvacrol.—A. Reychler.—For these three memoirs we must refer to the originals.

Series 3, Vols. vii. and viii., No. 3.

Action of Benzyl Chloride upon Non-Symmetric Metaxylinidine.—M. Jablin-Gonnet.—The salts of methylbenzylmetaxylinidine, such as the sulphate, the nitrate, and the hydrochlorate, are white and crystallise readily. Those of benzoylbenzylmetaxylinidine, such as the sulphate, the hydrochlorate, and the oxalate, crystallise less readily and are white, with the exception of the nitrate, which is yellow.

Fixation of Atmospheric Nitrogen by the Soil and by Plants.—Arm. Gautier and R. Drouin.—The authors first give a history of this controverted question. They examine separately (A) the progress of the assimilation of nitrogen, first in a fertile soil, devoid of vegetation, and (1) deprived of organic matter and iron; (2) the same soil mixed with salts or iron oxide; (3) in the same soil mixed with organic matter; (4) in the same soil mixed at once with organic matter and ferric oxide. (B) in the same soils with or without iron or organic matter, but after seeds have been sown in them. For determining the nitrogen they reject the processes of Kjeldahl and of Will-Varren-trap and adopt a modification of the method of Schloesing and Müntz. A tube of Bohemian glass of 1'20 metres in length and from 18 to 20 m.m. in internal diameter is sealed at its posterior extremity and slightly bent in the form of a gun-stock, which extends beyond the furnace grate by about 15 c.c. Into this tube they introduce (1) 18 grms. potassium chlorate melted and powdered and 6 grms. copper oxide (this mixture fills two-thirds of the bent part of the tube); (2) manganese carbonate for a length of about 10 c.m. intended to supply carbonic acid to sweep gases out of the tube at the beginning and at the end of the combustion; (3) cupric oxide in short tablets for the length of 12 c.m.; (4) 40 grms. of the soil to be analysed, not dried (its moisture having been determined in another specimen), carefully mixed in a bronze mortar with 180

grms. cupric oxide; (5) a long column of cupric oxide; (6) a good quantity of reduced copper, pulverulent and well broken up, extending for about 15 c.m. and filling the tube. Each of these portions is separated from the others by plugs of coarse fibres of asbestos, previously ignited. The tube is coated with copper foil from behind forwards, up to the column of reduced copper. It is placed in the furnace, and the air is expelled from it by repeatedly exhausting with a Gay-Lussac pump, liberating carbonic acid each time from the manganese carbonate, especially after the last stroke of the pump. The combustion is then effected in the ordinary manner. When all the part resting on the grate has been heated to redness, the potassium chlorate is moderately heated so as to liberate the oxygen until the reduced copper begins to be oxidised. This tube is then swept with a current of carbonic acid obtained by again heating the manganese carbonate. After the combustion the authors introduce into the gas receiver, placed over mercury and containing potassa-lye, a few c.c. of a concentrated solution of pyrogallol in case a trace of oxygen should have been introduced, and the volume of gas is then read off. The first series of experiments proves that the organic matter of the soil fix nitrogen independently of any vegetation. The second series shows that vegetation, especially leguminous plants, constitute a mode of the fixation of nitrogen. The authors are continuing their researches.

Synthetic Formation of Acetylene at the Expense of Bromoform.—P. Cazeneuve.—Already inserted.

The Chloriodide of Certain Organic Bases.—A. Picot and G. Krafft.—The authors describe the chloriodides of pyridine, of quinoline, piperidine, and trimethylamine.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Medical, 8.30.

TUESDAY, 26th.—Institute of Civil Engineers, 8.

— Royal Institution, 3. "The Sculpturing of Britain—its Later Stages," by Prof. T. G. Bonney, D.Sc., F.R.S.

— Royal Medical and Chirurgical, 8.30.

— Photographic, 8.

— Society of Arts, 8. "Australasia—its Progress and Resources," by Sir Edward Eraddon, K.C.M.G.

WEDNESDAY, 27th.—Society of Arts, 8. "Egyptian Agriculture," by Prof. Robert Wallace.

— Geological, 8.

THURSDAY, 28th.—Royal, 4.30.

— Institute of Electrical Engineers, 8.

— Society of Arts, 4.30. "Reorganisation of Agricultural Credit in India," by Sir William Wedderburn.

— Royal Institution, 3. "The Chemistry of Gases," by Prof. Dewar, F.R.S.

FRIDAY, 29th.—Royal Institution, 9. "The Physiology of Dreams," by Dr. B. W. Richardson, F.R.S.

SATURDAY, 30th.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Danreuther.

COAL-TAR COLOURS, *The Chemistry of.*

With special reference to their application to Dyeing, &c. By DR. R. BENEDIKT, Professor of Chemistry in the University of Vienna. Translated from the German by E. KNECHT, Ph.D. 2nd Edition, Revised and Enlarged, 6s. 6d.

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ROYAL INSTITUTION OF GREAT BRITAIN,
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PROFESSOR DEWAR, F.R.S., will on THURSDAY next, April 28, at Three o'clock, begin a Course of Four Lectures on "THE CHEMISTRY OF GASES." Subscription to this Course, Half-a-Guinea. To all the Courses in the Season, Two Guineas.

THE CHEMICAL NEWS.

Vol. LXV., No. 1692.

AN ATOMIC COLOUR CROSS.

By WILLIAM ACKROYD, F.I.C.

AN examination of some 450 coloured compounds and the distribution of their constituent elements in a table of the periodic classification of them, has revealed to me the fact that one may construct a cross in such a table which shall include one or more of the elements in nearly every coloured compound. Thus:—

	F 19. Cl 35'5.	O 16. N 14. S 32. P 31.
Cu 63. Co 59. Ni 59. Fe 56.	Mn 55.	Cr 53.
	Br 80. I 127.	Se 79. As 75. Te 125. Sb 120.

And if we add O, S, Se, Te, N, P, As, and Sb, I know of no coloured body which does not contain one or more of the elements in this system.

There is a rough approximation to an increase in geometric proportion in the average atomic weight of each of the sub-groups such a table divides itself into, which may have a bearing on the hypothesis that colour in compounds is some periodic function of atomic weight.

a.	2a.	4a.
$\frac{F+Cl}{2} = 27'5$	$\frac{Cu+Co+...+Cr}{6} = 57'5$	$\frac{Br+I}{2} = 103'5$
$\frac{O+S}{2} = 24$	do. = 57'5	$\frac{Se+Te}{2} = 102$
$\frac{N+P}{2} = 22'5$		$\frac{Sb+As}{2} = 97'5$

Borough Laboratory, Halifax,
March 27, 1892.

RESEARCHES ON THE METALS OF THE CERIUUM GROUP.*

TREATISE I.

By P. SCHÖTTLANDER.

THE great interest which the rare earths claim in recent times render it desirable in the first place to submit to a more thorough study the imperfectly known metals of the cerium group, and especially the complex of elements hitherto comprised under the name of didymium. As the older methods for separating the cerite metals are for the most part very tedious, and as the methods published

by Auer von Welsbach have been found in many respects far preferable, though in part dependent on certain conditions which the author has not always laid down with sufficient precision, I purpose considering some of the conditions which are required for the success of the different processes. On the theory of the latter only few indications can be given, as the explanation of several of the reactions which come into play must be reserved for future investigations.

As primary material there served a *cerium oxalicum purissimum* and a *cerium carbonicum purissimum* obtained in commerce, and alleged to have been obtained from oxalate and carbonate prepared from Norwegian orthite, from which a portion of the cerium had already been separated.

1.—Preparation of Pure Cerium Compounds, free from Lanthanum and Didymium.

According to Auer von Welsbach (*Monatshefte für Chemie*, 1884 and 1885, p. 508), the preparation is best founded upon the ready crystallisability of ammonium-ceric nitrate, and the inability of the other rare earths (with the exception of thorium) to form salts of the stage of oxidation corresponding to cerium dioxide. The attempt must therefore be made to prepare in the simplest manner a solution of the earths in nitric acid containing all the cerium present or the greatest possible proportion of it as a salt of the dioxide. The earthy oxalates dried at 100° dissolve very readily on digestion in heat with an excess of nitric acid of specific gravity 1.40. Vapours of hyponitric acid are given off and there remain nitrates. Still the cerium would be present only as cerous salt; this would be the simplest method if a suitable oxidising agent could be found which would convert the cerium of this solution into ceric nitrate. Possibly hydrogen peroxide or lead peroxide might be available. In default of such an oxidising agent the oxalates must be converted into oxides by strong ignition in presence of air.

Pure cerium oxalate, as, indeed, all pure cerium salts with an organic acid, pass on ignition in the air very readily into cerium dioxide, which is unchangeable at all temperatures and is quite insoluble in nitric acid, whether concentrated or dilute. But if the solution from which the oxalate was precipitated contained lanthanum and didymium along with cerium, the oxide obtained is the more soluble in nitric acid the larger the proportion of the two latter metals. In the solution there is, along with cerium dioxide, always a considerable proportion of cerous oxide, whether the latter is already contained as such in the mixture of oxides or whether it is formed from the cerium dioxide with loss of oxygen. The solubility of the oxide in nitric acid depends not alone on the quantity of lanthanum and didymium present, but to a great extent on its mechanical condition, and on the presence of foreign impurities such as silica, ferric oxide, alkaline salts, &c. If the proportion of cerium oxides in the mixture exceeds 50 per cent, and but little of the impurities above mentioned are present, it may often be brought into solution by covering the dry oxide in a state of fine division at once with 4 parts of nitric acid (containing 50 per cent HNO_3). There ensues a copious escape of oxygen and a violent reaction, the mixture becoming heated to ebullition, and in a few seconds everything is dissolved to a dark reddish yellow liquid. If, on the other hand, the oxide is moistened with water and then digested at 100° with strong nitric acid, the reaction is very tedious, and even after digestion with the constant addition of fresh portions of acid, it is not practicable to dissolve all the oxide, doubtless because there are formed basic salts in the latter case, but not in the former.

A mixture of oxides as it is obtained by working up most cerite minerals, e.g., cerite, is generally too rich in cerium to be dissolved in nitric acid as above mentioned. Hence, it is necessary firstly to eliminate the larger portion of the cerium, according to one of the old methods, e.g.,

* *Berichte der Deutsch. Chem. Gesell.*

that of Debray (*Comptes Rendus*, xcvi., p. 828), fusing the nitrates with potassium nitrate, and we may proceed as follows:—

The oxide is ground up in a mortar with $1\frac{1}{2}$ times its own weight of concentrated sulphuric acid; the mixture is transferred to a platinum capsule and heated gently whilst stirring until the mass has become yellow throughout and is converted into sulphate. When cold it is dissolved in a minimum of water without the application of heat; the liquid is allowed to deposit and the clear yellow solution is decanted off from the sediment.

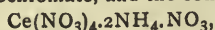
It is then poured into a large excess of soda-lye, which has been previously heated in a porcelain capsule; the liquid is boiled for some time; the mixture of hydroxides, which consists chiefly of cerium hydroxide, is repeatedly washed by decantation with boiling water in the capsule, then poured into a large glass, and washed with cold water by decantation until no trace of sulphuric acid can be detected in the washings by means of hydrochloric acid and barium chloride. The precipitate is then filtered off and dried at 100° . It is now readily soluble in nitric acid of specific gravity $1\cdot40$.

As it is advantageous to combine the preparation of a pure cerium salt with that of lanthanum and didymium salts free from cerium, it is preferable not to dissolve the mixed oxides in which the latter metals have been caused to accumulate directly in nitric acid, but to use for this purpose the basic cerium precipitate to be described below.

In presence of foreign impurities which may be derived from the minerals used or the reagents applied (lead from sulphuric acid, silica from the soda-lye, &c.), it is advisable not to evaporate at once the nitric solution of the basic cerium precipitate or of the hydroxide (prepared as directed) with an addition of ammonium nitrate until it crystallises, but to allow it to stand in the first place in the cold for 12 hours, when the nitrates of lead, copper, &c., which are sparingly soluble in strong nitric acid, separate out. The clear liquid is then decanted off, the necessary quantity of ammonium nitrate is added (when the oxide or its corresponding quantity of hydroxide is worked up three-quarters of the weight of the latter), and in presence of silica the liquid is evaporated to dryness. The liberated silica after dissolving the saline residue in dilute nitric acid is then removed by filtration through asbestos. Filtration through paper, which is practicable if the liquid is sufficiently diluted, must be avoided on account of its reductive action.

In working up the basic cerium precipitate, the separation of any silicate present is generally not needful. We dissolve 100 parts of the precipitate nearly completely, dried at 100° , in 265 parts of nitric acid of specific gravity $1\cdot40$; any lead nitrate present is allowed to crystallise out; 113 parts of water and 39 parts of ammonium nitrate are then added as a saturated solution at a temperature close upon ebullition, and the liquid is evaporated down upon the water-bath until crystals begin to form upon the surface of the blackish liquid. It is then allowed to cool slowly and is set aside for twelve hours.

The chief part of the ceric salt present in the solution is thus obtained in small, shining crystals of the colour of potassium pyrochromate, and the composition—



which are agglomerated in tufts and crusts of little consistence. After further evaporating the reddish-yellow mother-liquor we obtain in the first place some more crystals of the same salt. Subsequently there crystallises out an isomorphous mixture of the double ammonium cerium (cerous) lanthanum and didymium nitrates in large crystals generally compactly coalescent, and having a light yellow colour from inclosed mother-liquor. The

crystals have the composition $\text{R}(\text{NO}_3)_3 \cdot 2\text{NH}_4 \cdot \text{NO}_3 \cdot 4\text{H}_2\text{O}$. They may easily be separated from the crystals of the ceric salt, and along with the mother-liquor they may be

submitted anew to a process of separation by precipitation with oxalic acid, conversion into oxides, &c.

The ammonium-ceric nitrate is drained on a funnel with a cone of platinum wire gauze and dried upon unglazed porcelain under a bell-glass over quicklime and sodium hydroxide. For re-crystallising the salt it is best to use pure nitric acid free from chlorine and containing 40 per cent of HNO_3 ; 100 parts of the dried crystals are dissolved in a minimum of this acid, about 165 parts (99 parts nitric acid of specific gravity $1\cdot40$ and 66 parts of water) in a flask on the water-bath. The liquid is poured into a deep basin and evaporated until crystals appear. Re-crystallisation repeated three or four times is generally sufficient to remove from the salt the last traces of lanthanum and didymium. In this manner about 1400 grms. absolutely pure cerium double salt were obtained from the above material.

2.—Obtaining Salts of Lanthanum and Didymium free from Cerium.

If, as directed by Auer von Welsbach, we treat with moderately dilute nitric acid the finely-divided mixture of oxides of the cerite metals (obtained by precipitating with oxalic acid and igniting the oxalates), most of the lanthanum and didymium dissolve as nitrates, and if the proportions are properly selected and the reaction is sufficiently prolonged, all the cerium, to the last trace, passes into the precipitate absolutely insoluble in the liquid and consisting chiefly of basic nitrates. These assertions I can fully confirm, though if the mixture of oxides is very rich in cerium the reaction is very tedious and sometimes it does not take place, when again the presence of foreign impurities and other causes not easily ascertained play a part not unimportant. It is here advisable (as intimated in the former section) first to accumulate the lanthanum and didymium in the material operated upon and then proceed to the complete elimination of the cerium.

When by one or other method a solution has been obtained in which the proportion of the lanthanum and didymium oxides forms 50 per cent or more of the total earths, the separation of the earths is effected without difficulty if the following directions are accurately followed.

(To be continued).

ON THE RELATIVE DENSITIES OF HYDROGEN AND OXYGEN. II.*

By Lord RAYLEIGH, Sec.R.S.

(Concluded from p. 202).

IN the case of oxygen, the errors due to contamination (even with hydrogen) are very much diminished, and similar errors of weighing tell very much less upon the proportional agreement of the final numbers. A comparison of the actual results with the two kinds of gas does not, however, show so great an advantage on the side of the oxygen as might have been expected. The inference appears to be that the individual results are somewhat largely affected by temperature errors. Two thermometers were, indeed, used (on opposite sides) within the wooden box by which the globe is surrounded, and they could easily be read to within $1\cdot20^{\circ}\text{C}$. But in other respects the circumstances were unfavourable in consequence of the presence in the same room of the furnace necessary to heat the copper. An error of $\pm 0\cdot1^{\circ}\text{C}$. in the temperature leads to a discrepancy of 1 part in 1500 in the final numbers. Some further elaboration of the screening arrangements actually employed would have been an improvement, but inasmuch as the circum-

* From the *Proceedings of the Royal Society*, vol. 1. Read Feb. 18, 1892

stances were precisely the same for the two gases, no systematic error can here arise. The thermometers were, of course, the same in the two cases.

The experiments are grouped in five sets, two for oxygen and three for hydrogen. In each set the work was usually continued until the tap of the globe required re-greasing, or until, owing to a breakage or to some other accident, operations had to be suspended.

		Oxygen.	
1891.		Weight. Grm.	Bar. temp., ° F. Globe temp., ° C.
June 29		2'5182	70 20'85
July 2.. .. .		2'5173	69 20 60
" 4.. .. .		2'5172	67½ 19'75
" 6.. .. .		2'5193	70½ 21'40
" 9.. .. .		2'5174	64 17'60
" 10.. .. .		2'5177	65½ 19'05
Mean		2'51785	68 20

The six fillings were all independent, except that of July 6, when the bulk of the oxygen remaining from the previous filling was not removed. It so happens that this case shows the greatest discrepancy, but there seems to be no sufficient reason for rejecting it.

		Hydrogen.	
1891.		Weight. Grm.	Bar. temp., ° F. Globe temp., ° C.
July 31		0'15807	60½ 15'90
August 4		0'15816	65 18'00
" 6		0'15811	66½ 19'20
" 8		0'15803	65 18'15
" 11		0'15801	66 19'15
" 13		0'15809	68½ 20'10
Mean		0'15808	65 18

		Hydrogen.	
1891.		Weight. Grm.	Bar. temp., ° F. Globe temp., ° C.
September 22		0'15800	58 14'5
" 24		0'15820	61½ 16'3
" 28		0'15792	62 17'6
" 30		0'15788	63½ 18'1
October 2		0'15783	62 17'3
Mean		0'15797	61 17

		Hydrogen.	
1891.		Weight. Grm.	Bar. temp., ° F. Globe temp., ° C.
October 26		0'15807	55 13'30
" 28		0'15801	56 14'00
" 31		0'15817	50 10'95
November 3		0'15790	53½ 12'10
" 5		0'15810	55 12'00
" 7		0'15798	50 10'70
" 10		0'15802	48 9'30
" 13		0'15807	55½ 12'70
Mean		0'15804	53 12

		Oxygen.	
1891.		Weight. Grms.	Bar. temp., ° F. Globe temp., ° C.
November 31		2'5183	53 12'15
December 3		2'5168	56 13'55
" 5		2'5172	56½ 14'15
" 7		2'5181	58½ 14'70
" 8		2'5156	51 11'15
Mean		2'5172	55 13

In almost every case the weight of the globe full is compared with the mean of the immediately preceding and following weights empty. The numbers recorded in the second column are derived from the readings of the balance by the introduction of corrections—

(1) For the errors of the weights themselves, found by a systematic comparison, only relative values uncorrected for buoyancy being required.

(2) For the deviation of the mean (there were two barometers) barometric reading at the time of filling from 30 inches (as read upon the vernier).

(3) For the deviation of the temperature of the barometers (column 3) from 60° F.

(4) For the deviation of the temperature of the gas (as read upon the thermometers) from 12° C.

As an example I will take in detail the calculation for the hydrogen filling of October 26. After the evacuation of October 24, the working globe (14) with its compensating volume piece and 0'4778 gm. stood on the left of the balance with globe (11) on the right. The position of equilibrium of the pointer, as determined after four different releasements, each observed in the usual manner, was 19'02 scale divisions. In like manner, after the evacuation of October 27, with the same weights in use, the equilibrium position of the pointer was 18'46. After the filling of October 26, the weights associated with (14) were 0'3220 gm., instead of 0'4778; and the pointer reading was 20'08. So far as the weights are concerned, the value of the hydrogen would be 0'4778—0'3220, or 0'1558 gm.; but to this we must add a correction corresponding to 1'34 scale divisions, being the difference between 20'08 and ½(19'02+18'46). At the time in question, the value of a scale division was 0'00020 gm., so that we obtain—

$$0'1558 + 0'00027 = 0'15607.$$

The particular weights in use on this occasion were such that no correction is necessary in order to allow for their errors.

The mean barometer reading at the time of filling was 29'742, so that the factor required on this account is 30 : 29'742. The correction for temperature of gas is from 13'3 to 12°.

$$\begin{array}{rcl} \text{Log } 0'15607 & \dots & = 1'19332 \\ \text{For barometer} & \dots & 0'00375 \\ \text{,, temperature} & \dots & 0'00198 \\ \hline \text{Log } 0'15814 & \dots & = 1'19905 \end{array}$$

To this a correction for the temperature of the barometer has still to be applied. For 1° F. the correcting factor is (1—0'000089), or for 5° F. (1—0'000445). From 0'15814 we are thus to subtract 0'00007, giving the tabular number 0'15807.

A further minute correction to the mean of each set may be made for the temperature of the glass. A warm globe is larger than a cold one, and consequently holds more gas. If we suppose that the volume expansion of the glass per degree C. is 0'000025, we find, corrected to 12° C.—

		Hydrogen.		Corrected to 12°.
1891		Weight. Grm.	Bar. temp., ° F. Globe temp., ° C.	Grm.
July		0'15808	65 18	0'158056
September		0'15797	61 17	0'157950
October		0'15804	53 12	0'158040
Mean		—	60 16	0'158015

		Oxygen.		Corrected to 12°.
1891.		Weight. Grms.	Bar. temp., ° F. Globe temp., ° C.	Grms.
June		2'51785	68 20	2'51735
November		2'51720	55 13	2'51713
Mean		—	61½ 16½	2'51724

The means here exhibited give the weights of the two gases as they would be found with the globe at 12° C., and the barometers at 60° F. and at 30 inches. The close agreement of the mean temperatures for the two gases shows how little room there is for systematic error dependent upon imperfections in the barometers and thermometers. But the results still require modification before they can be compared with the view of deducing the relative densities of the gases.

In the first place there is a systematic, though minute, difference in the pressures hitherto considered as corresponding. The terminal of the blow-off tube is 33 inches below the centre of the globe at the time of filling. In the one case this is occupied by hydrogen, and in the other by oxygen. If we treat the latter as the standard, we must regard the hydrogen fillings as taking place under an excess of pressure equal to $\frac{1}{16}$ of the weight of a column of oxygen 33 inches high; and this must be compared with 30 inches of mercury. Hence, if we take the sp. gr. of oxygen under atmospheric conditions at 0.0014, and that of mercury at 13.6, the excess of pressure under which the hydrogen was collected is as a fraction of the whole pressure—

$$\frac{33}{30} \cdot \frac{15}{16} \cdot \frac{0.0014}{13.6} = 0.000106;$$

and $0.000106 \times 0.158 = 0.000017$. This, then, is what we must subtract from the weight of the hydrogen on account of the difference of pressures due to the gas in the blow-off tube. Thus—

$$H = 0.157998, \quad O = 2.51724.$$

(These numbers are not quite comparable with those given in the former communication, inasmuch as the standard temperature then used for the barometers was 55° F. Reduced so as to correspond to 60°, the former numbers become—

$$H = 0.15797, \quad O = 2.5174.$$

The agreement is satisfactory, especially when it is remembered that both gases were prepared by different methods in the two sets of experiments.—Feb. 17.)

But there is still another and a more important correction to be introduced. In my former paper it was shown that when the weighings are conducted in air the true weight of the gas contained in the globe is not given by merely subtracting the weight of the globe when empty from the weight when full. When the globe is empty, its external volume is less than when full, and thus, in order to obtain the true weight, the apparent weight of the gas must be increased by the weight of air whose volume is equal to the change of volume of the globe.

In order to determine the amount of this change of volume, the globe is filled to the neck with recently boiled distilled water, and the effect is observed upon the level in the stem due to a suction of, say, 20 inches of mercury. It is not advisable to carry the exhaustion much further for fear of approaching too nearly the point at which bubbles of vapour may be formed internally. In the earlier experiments, described in the preliminary note, the upper surface of the liquid was in the stem of the globe itself (below the tap), and the only difficulty lay in the accurate estimation of a change of volume occurring in a wide and somewhat irregular tube. The method employed was to produce, by introduction of a weighed quantity of mercury, a rise of level equal to that caused by the suction.

The advantage of this procedure lay in the avoidance of joints and of the tap itself, but, for the reasons given, the readings were not quite so accurate as might be desired. I wished, therefore, to supplement, if possible, the former determination by one in which the change of volume occurred in a tube narrower and of better shape. With this object in view, the stem of the globe was prolonged by a graduated tubular pipette attached with the aid of indiarubber. The tubes themselves were treated

with gutta-percha cement, and brought almost into contact. It had hardly been expected that the joint would prove unyielding under the applied suction, but it was considered that the amount of the yielding could be estimated and allowed for by operations conducted *with tap closed*. The event, however, proved that the yielding at the joint was scarcely, if at all, perceptible.

The pipette, of bore such that 16 c.m. corresponded to 1 c.c., was graduated to 0.01, and was read by estimation to 0.001 c.c. In order the better to eliminate the changes due to temperature, readings under atmospheric pressure and under a suction of 20 inches of mercury were alternated. On January 28, 1892, a first set gave $0.648 - 0.300 = 0.348$, a second gave $0.6645 - 0.316 = 0.3485$, and a third gave $0.657 - 0.326 = 0.331$. Similar operations with tap closed* gave no visible movement.

The result of the day's experiments was thus 0.3485 for 20 inches, or 0.523 for 30 inches, suction. Similar experiments on January 28, at a different part of the graduation, gave 0.526. On this day the yielding with tap closed was just visible, and was estimated at 0.001. As a mean result we may adopt 0.524 c.c. The graduation of the pipette was subsequently verified by weighing a thread of mercury that occupied a measured length.

A part of the above-mentioned volume is due to the expansion of the water when the pressure is relieved. We may take this at 0.000047 of the volume per atmosphere. The volume itself may be derived with sufficient accuracy for the present purpose from the weight of its oxygen contents. It is $2.517/0.00137$, or 1837 c.c. The expansion of the water per atmosphere is thus 0.000047×1837 , or 0.087 c.c. This is to be subtracted from 0.524, and leaves 0.437 c.c. This number applies strictly to the volume enclosed within the glass, but the change in the external volume of the globe will be almost the same.†

The correction now under consideration is thus the weight of 0.437 c.c. of air at the average temperature of the balance room. The density of this air may be estimated at 0.00122, so that the weight of 0.437 c.c. is 0.000533 grm. This is the quantity which must be added to the apparent weights of the gases. The former estimate was 0.00056 grm. The finally corrected weights are thus—

$$H = 0.158531, \quad O = 2.51777;$$

and for the ratio of densities we have—

$$15.882.$$

This corresponds to a mean atmospheric condition of pressure and temperature.

If we combine the above ratio of densities with Prof. Morley's ratio of volumes, viz., 2.0002:1, we get, as the ratio of atomic weights, 15.880.

If we refer to the table we see that the agreement of the first and third series of hydrogen weighings is very good, but that the mean from the second series is decidedly lighter. This may have been in part fortuitous, but it is scarcely probable that it was so altogether. Under the circumstances we can hardly reckon the accuracy of the final results as closer than $\frac{1}{3000}$.

A word should perhaps be said upon a possible source of systematic error, viz., mercury vapour. There is no doubt that hydrogen passed over mercury takes up enough to cause a slow and superficial, but quite distinct, discolouration of sulphur, over which it subsequently flows. In the experiments here recorded, the gas did not, indeed, flow over mercury in mass, but, inasmuch as mercury was

* For greater security the tap was turned while the interior was under suction.

† For a spherical shell of glass of uniform thickness and with elastic constants following Poisson's law, the ratio of the difference of the internal and external expansion to either of them is $\frac{4t}{3a}$, where t is the thickness of the shell and a the mean radius. In the present application the value of $\frac{4t}{3a}$, deduced from the measured circumference and from the weight of glass, is about 120.

(Perhaps an arrangement in which the external volume is directly measured would have been preferable. No allowance for expansion of water would then be needed.—Feb. 17.)

used to secure the tightness of some of the joints, it is difficult to feel sure of its absence. Again, in evacuations conducted with a mercury pump, can the vacuum be regarded as free from mercury vapour, which, it must be remembered, would not show itself upon the gauge of the Töpler? If both the hydrogen and the "vacuum" were saturated with mercury vapour, the result of the weighings would, according to Dalton's law, be free from its influence. The same may be said of any volatile impurity arising from the grease* upon the stop-cocks. As the matter stands, the results must, I think, be regarded as affected with a possible error amounting to a fraction of the weight of mercury vapour at the temperatures employed. But this is probably a very small quantity.

According to Hertz,† the vapour pressure of mercury at 15° C. would be about 0.001 m.m. If this be correct, the weight of mercury vapour in an atmosphere of hydrogen would be as a fraction of the latter—

$$\frac{0.001}{760} \times 200 = \frac{1}{3800}.$$

It appears that in an investigation of hydrogen aiming at an accuracy of 1/10,000, the question of mercury vapour requires very careful consideration.

The accompanying table of results found by various experimenters may be useful for comparison:—

Name.	Date.	Atomic weighrs	Densities.
Dumas	1842	15.96	—
Regnault	1845	—	15.96
Rayleigh	1888	—	15.884
Cooke and Richards :	1888	15.869	—
Keiser	1888	15.949	—
Rayleigh	1889	15.89	—
Noyes	1890	15.896	—
Dittmar	1890	15.866	—
Morley	1891	15.879	—
Leduc	1891	—	15.905
Rayleigh	1892	—	15.882

In conclusion, I must express my obligations to Mr. Gordon, who has assisted me throughout. The work has been unusually tedious, partly from its inherent nature, requiring as it does a certainty of 0.1 m.grm. in the weighings, and still more from the constant liability to accidents, which may render nugatory a large amount of preparatory work.

DIFFERENCES IN THE DETERMINATION OF REVERTED PHOSPHORIC ACID BY THE OFFICIAL METHOD OF ANALYSIS.‡

By CHARLES GIBSON.

HAVING found it utterly impossible to make my analyses for the amounts of reverted phosphoric acid in several consignments of high-grade aluminic phosphate agree within several per cent with those of Messrs. Stillwell and Gladding, of New York, both of us using the official method, I proceeded to investigate by numerous experiments. The conclusions I have arrived at, and the reasons therefor, together with a few of the results I and others have obtained, I now propose to lay before this Association.

When this material was first placed on the market my company, thinking perhaps we could use it profitably and advantageously in other respects in our factory, purchased a few consignments; and at the suggestion of the vendors we readily agreed to settle on the analyses of

Messrs. Stillwell and Gladding, who were chemists of great eminence; and the fact of their using the official method of analysis contributed in no small degree to our ready assent. Their analyses of the different consignments, which they have since informed me were by the official method strictly as to time, temperature, &c., were checked, by me, not using the official method, however, but using the method which I use in controlling the work in the factory—the alkaline citrate method of Joulie—our results invariably agreeing to within one-tenth of 1 per cent. Goods were in due time made up with this material as one of the ingredients, and samples drawn and submitted to the chemists of the various States where they were likely to be sold. On the reports from the State chemists coming to hand we were surprised to find that they all, without a single exception, gave a very much lower percentage of available P₂O₅ than we had a right to expect, amounting to about 15 per cent on the ton of aluminic phosphate used.

Investigation proved that there had been no mistake in the weighing out of the materials. The proportions were found to be correct, and nothing of a retrograde nature could be discovered, at least with the Joulie method of analysis. But, in using the official method on the prepared goods, I obtained results which agreed completely with those of the State chemists. Evidently there was something wrong somewhere, and an analysis of a sample drawn from one of the consignments of aluminic phosphate (using the official method, instead of the alkaline method) indicated in which direction the trouble lay. This analysis gave results of about 15 per cent available P₂O₅ less than had been found by Messrs. Stillwell and Gladding. Repeated analyses with the same and other solutions failed to change this, and an examination by the official method showed the same state of things with regard to every consignment we had received. Through the kindness of two of the State chemists, the Hon. M. A. Scovell, of Kentucky, president of this association, and Professor H. A. Huston, of Indiana, I have been able to verify the correctness of my results, at least as far as one consignment is concerned, as the following will show:—

Stillwell and Gladding found 34.73 per cent available P₂O₅; total, P₂O₅, 47.04 per cent.

Mr. Scovell, 20.31 per cent available P₂O₅; total P₂O₅, 44.25 per cent.

Professor Huston, 19.40 per cent available P₂O₅; total P₂O₅, 45.46 per cent.

My own, by official method, 19.70 per cent available P₂O₅; total P₂O₅, 46.7 per cent.

My own, by alkaline method, 34.74 per cent available P₂O₅; total P₂O₅, 47.0 per cent.

This matter thus assumed for us a serious aspect, for here we were both buying and selling on analytical results obtained by the official method, and yet, from a cause over which we had not the slightest control, we were subjected to a financial loss of very serious proportions, amounting to between 10 dollars and 12 dollars per ton of aluminic phosphate used.

Continuing the investigation with a view of finding whether or not this serious evil could be avoided, I found that infinitesimal variations in the preparation of the ammonia citrate solution of the official method very materially changed the results in the determinations of reverted P₂O₅ in this material. Although in the preparation and use of the ammonia citrate solution the directions as laid down in *Bulletin* No. 24, page 224, were followed with the utmost care, I was totally unable to prepare two solutions that would give anything like concordant results; and even with the same solution they were anything but uniform. The cause of this I found to be owing to very slight unavoidable variations in the composition of the ammonia citrate solution. I also found that the slightest inclination to acidity very largely affected the insolubility of this material. Now, from the mode of its preparation, it is evident that a perfectly

* Composed of vaseline and beeswax.

† *Wied. Ann.*, xvii, p. 199.

‡ From the *Proceedings of the Seventh Annual Convention of the Association of Official Agricultural Chemists*, Washington.

neutral solution of citrate ammonia is practically unattainable, although the variations from neutrality must of necessity be of the minutest kind if proper care is used. These variations must either incline to alkalinity or acidity, but a little consideration would lead to the belief that, in almost every case (except where precautions are taken to insure the reverse) the inclination is to acidity.

I therefore prepared a solution of citrate of ammonia in the same manner as I conceived the majority of analysts, who did not know of the effect of this acidity, might prepare it. The directions in *Bulletin* No. 24, page 224, were followed with great care, and neutrality made by the addition of ammonia hydrate until the solution ceased to show acidity with blue litmus paper of great delicacy. Red litmus paper of great delicacy was also unaffected. I tried rosolic acid, but could do no better. We will call the solution A. Another solution, B, was made by adding ammonia hydrate to a portion of A until it showed a very faint alkalinity with delicate red litmus paper. The quantity of ammonia hydrate necessary to do this was about 1 cubic centimetre of a solution of the strength of 22° Baumé, to 1 litre of the A solution. I also prepared, with a view of obtaining a comparison of the two methods, a solution, C, according to the directions of M. H. Joulie, making it, as directed, strongly alkaline.

Before trying these solutions on the aluminic phosphate, I was curious to see what differences in effect, if any, they would produce on calcium phosphate. One grm. of ground South Carolina rock containing 27 per cent P_2O_5 was taken in each experiment, and digested without attempting to remove the small quantity of water-soluble (if indeed any were present). The official method was carried out strictly as to time, temperature, &c., with regard to A and B; and Joulie's directions in everything except time, which was only one-half hour instead of one hour with regard to C, no heat being applied in this case, it being digested at the temperature of the laboratory. The following results were obtained in per cent of reverted P_2O_5 —

A.	B.	C.
1.01	0.75	0.73
0.90	0.73	0.74
0.83	0.76	0.77
Mean ..	0.913	0.746

Three experiments were now made in every respect the same as above, except that all were digested one hour, the time specified in Joulie's method, and the following results in per cent of reverted P_2O_5 were obtained:—

A.	B.	C.
1.85	0.787	0.73
1.83	0.74	0.78
1.86	0.76	0.77
Mean ..	1.846	0.761

Five different portions of 1 grm. each were now digested in C for four hours, and I obtained the following percentages of reverted P_2O_5 : 0.71, 0.78, 0.79, 0.70, 0.75. Mean of the five: 0.746, or the same as B and C gave when the substance was digested only half an hour.

There is great significance in the results thus obtained. The continuous dissolving action of the solution A is apparent, while both the B and C solutions cease to act as soon, apparently, as all the available P_2O_5 has been dissolved, which is within the first half hour; and an indefinite extension of the time of digesting, especially in the case of the C solution, seems to produce no further effect. Thus solutions B and C have been prepared, which, contrary to the generally accepted belief, will not go on continuously dissolving out P_2O_5 from calcium phosphate as long as any remains undissolved, provided enough time is allowed; and we have here (if, by further

experiment, this is found by others to be true) a true measure of the availability of a phosphate, or at least a means of separating more sharply than we have hitherto been able to do soluble calcium phosphates from insoluble; and, with such a solution, which can be made by a very slight modification of the present official solution, the time element in the official method would cease to be an essential, as it is now, and would, in all probability, give much more accurate results, as well as conduce, more than anything else, to constancy and uniformity of results. From these experiments we perceive that a solution inclined to acidity, like solution A, tends, on calcium phosphate, to err on the side of too high a percentage of reverted phosphoric acid. The error is probably very small, but still that is the tendency. When, however, such a solution is used on aluminic phosphate, the reverse is the case to such an extent as to make the official method utterly worthless for the analysis of this material.

One grm. of the aluminic phosphate containing 47 per cent P_2O_5 , with 34.74 per cent available P_2O_5 , according to Stillwell and Gladding, was digested in each of the solutions A, B, and C, strictly following as to time, temperature, &c., the official method with A and B; and Joulie's method, except as to time, which was one-half hour, instead of one hour, with C. The water soluble, being insignificant in amount, was not removed before digesting. The following are the results obtained:—

A.	B.	C.
19.80	31.24	26.18
19.90	33.44	27.63
19.63	30.31	26.92
Mean ..	19.77	31.66

One grm. of the material was now treated in every respect the same as in the last experiments, except that the digestion was one hour instead of half an hour in all cases, and gave the following results, in per cent available P_2O_5 :—

A.	B.	C.
31.48	34.68	34.74
32.11	34.79	34.72
30.59	34.73	34.74
Mean ..	31.39	34.73

It seems incredible that two solutions differing so very slightly in composition as do the solutions A and B should give such widely divergent results, the difference between the mean of the three results obtained by solution A and the mean of the three obtained by solution B by digesting half an hour, being no less than 11.89 per cent available P_2O_5 . The lack of concord in the results obtained by each solution separately, together with the wide differences in the means of the results obtained from the three solutions, suggest the conclusion, however, that in the case of each solution, the official time (half an hour) was insufficient to dissolve the material.

By digesting one hour, concordant and uniform results are obtained by solutions B and C. The results from A are still very much lower than B, although the difference is not so great as it was in the previous experiments. I found that the material was capable of being almost completely dissolved in all three solutions, if sufficient time was given.

(To be continued.)

On Metaphenyltoluene.—G. Perrier.—Of the three phenyltoluenes theoretically possible, the ortho-compound has been studied by Barbier and the para-compound by Carnelley and Thomson. To obtain the meta-compound the author causes metabromotoluene to act upon phenylbromide in presence of an excess of sodium.—*Bull. Soc. Chim. de Paris*, No. 6, 1892.

ON THE
APPLICATION OF THE SAFETY LAMP
TO THE DETECTION OF BENZOLINE VAPOUR
AND OTHER INFLAMMABLE VAPOURS
IN THE AIR.*

By FRANK CLOWES, D.Sc. (London),
Professor of Chemistry, University College, Nottingham.

SINCE the vapour of benzoline and of petroleum spirit, when mixed with air, may become dangerously explosive and inflammable, it is found necessary to employ safety-lamps instead of naked lights to illuminate spaces which may contain such a mixture. The safety-lamp should accordingly be used in the neighbourhood of the oil tanks in petroleum-carrying steamers, in petroleum stores, and in chambers in which processes are carried on which involve the use of light petroleum oil.

The suggestion naturally occurs that the safety-lamp used in these places should be applied to ascertain whether the amount of inflammable vapour present in the air is sufficient to give rise to danger if it should come into contact with the naked flame; in other words, to ascertain if the space is sufficiently ventilated. Experiments were accordingly undertaken to discover whether benzoline vapour would give rise to a "cap" over the flame of the safety lamp, and if a "cap" appeared, to discover how small a proportion of the vapour could be detected in air by this flame-cap test. Since the hydrogen flame in the safety-lamp, and the benzoline flame in Ashworth's modified lamp, had been found to be most convenient for the formation of visible "caps," these lamps were employed in the experiments; and the test chamber previously described was employed for exposing the lamps to mixtures in varying proportions of benzoline vapour with air.

Since benzoline is a mixture of liquids, and is therefore not of invariable chemical composition, no attempt was made to ascertain the actual percentage of the vapour present in the air. The percentages of vapour, even if known and identical in amount, would probably have different effects when derived from different samples of benzoline, or even when derived from the same samples under different conditions. Accordingly an approximate determination only was made of the amount of further dilution with air which an explosive or inflammable mixture might undergo before the "cap" it produced over the safety-lamp flame ceased to be easily visible.

A large gas-holder was filled with air which had bubbled through benzoline, and was thus charged with the vapour at the ordinary temperature, in the same way as air would be charged with the vapour from the evaporation of stored benzoline. This mixture was inflammable when kindled in the open air. Varying proportions of this mixture with additional air were then prepared, and the effect was ascertained of introducing a flame into them. It was found that a mixture of 1 volume of benzolised air with 4 volumes of air was violently explosive. When the proportion of air was increased from 4 to 7 volumes the mixture was still inflammable, and when the air was increased to 9 volumes the mixture ceased to be inflammable. Mixtures of the same benzolised air were then made in the test chamber with still larger proportions of air, and the appearance of the safety-lamp flames was examined in these mixtures, with the results shown in table.

The results of these experiments showed that the 10 m.m. hydrogen flame in the Ashworth safety-lamp will detect a quantity of benzoline vapour in air which is only $\frac{1}{16}$ th that of the explosive proportion, and $\frac{1}{16}$ th of that which is inflammable when mixed with air. The benzoline flame shows a very small but distinct "cap" when the amount of benzoline vapour is $\frac{1}{16}$ th that requisite for production of an explosive mixture, and $\frac{1}{16}$ th that will yield an inflammable mixture.

Proportion of benzolised air to air in mixture.	Behaviour of the mixture with a naked flame.	Appearance of the hydrogen "cap" over safety-lamp flame in the mixture.
1 : 4	Violently explosive.	
1 : 5	Burns rapidly, and would probably be explosive if fired in large quantity.	
1 : 6		
1 : 7		
1 : 8	Burns around a flame only.	
1 : 9	Non-inflammable.	
1 : 23	"	52 m.m. "cap."
1 : 36	"	43 " " " with benzoline flame.
1 : 72	"	4 " " " " "
1 : 144	"	31 m.m. "cap."
		22 " " "

Further experiments of a similar kind are being made with the vapour of alcohol and of ether.

I have to acknowledge with pleasure the valuable manipulative skill and fertility of resource of W. T. Rigby, who has assisted me in carrying out the experiments with the test chamber.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 30th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

THE PRESIDENT delivered an Address, of which the following is an abstract:—

The number of Fellows of the Society is 1855, including 30 foreign members, 120 Fellows having been admitted during the year.

The Society has to deplore the loss of two veteran foreign members, Hermann Kopp and Jean Servais Stas. The Treasurer has undertaken to give an account of the work of the former, and to sketch the modern development of his ideas in a lecture to be delivered during the coming session. It is hoped that in like manner justice may be done to the work of Stas by one of the Fellows specially qualified to deal with such a subject.

The following tabular statement gives the numerical position of the Society:—

Number of Fellows (Anniversary, March, 1891) ..	1754
Since elected and paid admission fees	120
	1874
Removed on account of arrears	18
Withdrawn	18
Deceased	13
	49
Present Number of Fellows	1825
Number of Foreign Members (1891) ..	32
Deceased	2
	30
Present number of Foreign Members	30

13 Fellows have died within the year:—Dr. J. H. Abrahall, Dr. A. J. Bernays, Chas. Heisch, H. J. Hardy, T. H. Hills, J. S. Jackson, J. B. Mackintosh, C. McNally, J. W. Pratt, Dr. Redwood, A. J. Shilton, Dr. Tidy and P. H. Wright.

18 Fellows have withdrawn:—H. H. Bunting, W. L. Clarke, W. Y. Dent, Rev. G. R. Faulkner, Robt. Ferguson, Thos. Hilditch, Rev. T. Lindsay, Wm. Robinson, J. B. Readman, W. H. Reid, Chas. T. Sprague, George

* A Paper read before the Royal Society.

Sutcliffe, C. H. Sieber, Samuel D. Wills, J. C. Watson, W. C. Wise, Prof. E. Marks, and D. T. C. Charles.

18 Fellows have been removed on account of arrears: T. S. Conisbee, W. Crossley, Albert Cobb, Ed. Dawson, Chas. Hulke, Wm. Houlding, H. E. J. Irons, A. J. G. Lowe, Rev. S. Langdon, Eberhard Luttgen, Jas. Mayne, E. W. Parnell, Wm. Rupp, S. A. P. Szczepanowski, Edward de Souza, Arthur Stanley, W. B. Turner, and T. E. Towerson.

No fewer than 128 papers have been read, the largest number on record. The 1891 volume of the *Chem. Soc. Trans.* contains 95 original papers, occupying 1100 pages, while the Abstracts occupy 1564 pages.

At the commencement of the winter session Professor Attfield brought under the notice of the Council his proposal for establishing a Chemists' Benevolent Fund. A Committee was appointed to consider this proposal, and eventually they presented their Report (see p. 157), stating that it represented their unanimous opinion.

This Report was considered and adopted by the Council, and by their unanimous vote it was resolved:—

"That the Report of the Committee on the proposed institution by the Chemical Society of a 'Chemists' Benevolent Fund' be received and entered upon the Minutes.

"That in view (a) of the claims of scientific chemists on the Relief Fund of the Royal Society; (b) of the difficulties that would attend the establishment and satisfactory administration of a separate Fund by the Chemical Society; and (c) of the conditions affecting the particular scheme, Prof. Attfield's proposal for the establishment of a 'Chemists' Benevolent Fund,' in connection with the Chemical Society, be not entertained.

"That a copy of this Resolution be forwarded to Prof. Attfield, with an expression of thanks to him personally for the unsparing efforts he has made in the matter, and to the promised contributors to the suggested Fund for their generously proffered support thereto."

A Committee of the Council have had under consideration the question of the entire rearrangement, ventilation, and lighting of the meeting room, and with the co-operation of Professor Ayrtton and Mr. Martin L. Saunders (architect) have prepared a scheme which is now under the consideration of Her Majesty's Office of Works; if approved, this will be carried into effect during the long vacation.

In the remainder of his Address, the President dwelt chiefly on the work which is being done on the border lines of chemistry proper—referring both to that by which an approach is gradually being made towards understanding the chemistry of Nature's organic laboratory; and to the application of mathematical and physical methods of inquiry to the solution of chemical problems.

Sir Henry Roscoe proposed a vote of thanks to the President, coupled with the request that he allow his Address to be printed. Dr. GLADSTONE seconded the motion, which was carried by acclamation. The President having thanked the meeting,

Prof. THORPE, the Treasurer, gave an account of the balance sheet, which he laid before the Society duly audited. The receipts had been:—By admission fees and subscriptions, £3545; by sale of Journal, £408 7s. 4d.; and by dividends on invested capital, £367 12s. 10d. The expenses had been:—On account of the Journal, £2798 15s. 10d.; on account of the *Proceedings*, £159 14s. 5d.; on account of the Library, £277 6s. 2d.; the total expenditure being £3989 1s. 6d. Grants amounting to £406 5s. 4d. had been made to Fellows from the Research Fund during the year. As illustrating the growth of the Society's work, the Treasurer mentioned that whereas the expenditure on the Journal had been only £1733 11s. 10d. in 1882, in 1887 it had risen to £2026 16s. 9d., and this year amounted to £2798 15s. 10d. He anticipated that the proposed alterations and re-decorations of the Society's rooms during the coming long vacation

would absorb nearly £1000 of the balance now at the bank.

Mr. David HOWARD proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Prof. E. FRANKLAND.

Sir Henry ROSCOE having asked for information with reference to the Report of the Jubilee Meeting, and with regard to the Learned Societies' Registration Bill, both items of charge in the balance sheet, Dr. ARMSTRONG said that the former was in hand, and would ere long be ready for issue; unfortunately they had been unable to induce any Government Department to take charge of the Registration Bill, and he feared that there was but little chance of getting it brought forward unless promoted as a private measure.

Mr. CASSALL, after a reference to the cost of printing the suggested alterations in the bye-laws, which he supposed was included in the cost of printing the *Proceedings*, asked the President whether he had received a letter, and was prepared to consider the request therein made that he would inspect the documents in which a number of Fellows of the Society had expressed their wishes with reference to the suggested alterations in the bye-laws.

The President replied that he had received a letter signed by Dr. Teed and Mr. Cassall, and that he could only say that a letter from even one Fellow of the Society would meet with every consideration from him.

The vote of thanks to the Treasurer having been passed, the Treasurer proposed a vote of thanks to the Auditors, mentioning that he was much indebted to Mr. Tutton for his assistance in connection with the accounts. Prof. RAMSAY seconded the motion, which was unanimously adopted, and acknowledged by Mr. DYER.

Prof. ODLING then proposed a vote of thanks to the Council and Officers, including the Editors, Abstractors, and Librarian. Mr. CARTEIGHE supported the motion, which was adopted. Dr. ARMSTRONG and Mr. GROVES having replied,

Scrutators were appointed, and a ballot was then taken for the election of Officers and Council for the ensuing year; the following were subsequently declared elected.

President—Dr. A. Crum Brown, F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—A. Vernon Harcourt, F.R.S.; W. N. Hartley, F.R.S.; John Pattinson; William Ramsay, F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries—H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council—Henry Bassett; Norman Collie, Ph.D.; Harold Dixon, F.R.S.; John Ferguson, M.A.; R. J. Friswell; John Heron; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; John A. Voelcker, Ph.D.; W. P. Wynne, B.Sc.

Correction of a "Note on a New Acid from Camphoric Acid." By W. H. PERKIN, jun., F.R.S. (*ante*, p. 165).

The author desires to express regret that he had overlooked a previous paper by Damsky (*Ber.*, 1887, 2964), in which an account is already given of the acid recently described by him as new.

April 7th, 1892.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. Frederick William George Blyth, Clifton Wood, Clifton, Bristol; George Fitz-Brown, Ditton, Widnes; Walter William Duffield, 24, Ursula Street, Battersea, S.W.; Walter N. Edwards, 4, Herne Hill Road, Camberwell, S.E.; Harold F. Hills, 149, Bow Road, London, E.; John H. B. Jenkins, 23, Harding Street, New Swindon; Albert Morris, 115, Hope Street, Dukinfield; Joseph Chas. Mulrenan, 45, Manor Road, Stoke Newington, N.; Wm. Herbert Stables, B.A., Glebe House, Kirkstall, Leeds; Laurence John de Whalley, B.Sc., 26, Park Place, Greenwich.

Of the following papers, those marked * were read:—

*1. "The Separation of Arsenic, Antimony, and Tin." By JOHN CLARK, Ph.D.

The mixed sulphides of arsenic, antimony, and tin, obtained in the ordinary course of analysis are dissolved in a strong solution of ferric chloride in chlorhydric acid, and the arsenic is distilled off and weighed as trisulphide. The residual liquid contains the antimony as trichloride, and the tin as stannic chloride, also ferrous and ferric chlorides. The author corroborates Loveton's statement that antimony and tin can be separated by taking advantage of the difference in solubility of their sulphides in solutions of hydrogen chloride of certain strengths, but thinks the proportion of acid should be reduced from a half to a third, to ensure the complete precipitation of the antimony, and to avoid the necessity of filtering through cotton-wool. He recommends a combination of Loveton's and F. W. Clarke's processes, and without removing the iron salts he precipitates the antimony with hydrogen sulphide in a tepid solution containing from $\frac{1}{4}$ to $\frac{1}{2}$ of its volume of chlorhydric acid and a considerable quantity of oxalic acid. The precipitate, which is free from tin, is washed first with water, then with alcohol, and finally with carbon bisulphide, and weighed as Sb_2S_3 after being heated at a temperature of about 130° to ensure the complete expulsion of water. He considers this temperature sufficiently high to dry the Sb_2S_3 . He points out that when Sb_2S_3 is dried at 130° it suffers little or no further loss in weight till it is raised to the temperature at which it is converted into the black sulphide, and his experiments indicate that the loss in weight observed at this stage is not due to water but to oxidation, as after heating between 200° and 230° for several days there was a continuous loss, the black sulphide becoming brown, and it was found by analysis to consist chiefly of oxide of antimony.

When the Sb_2S_3 precipitate is large it is necessary, after drying, to digest it in carbon bisulphide to extract the whole of the sulphur. To obviate this objection the author reduces the excess of ferric chloride with thin sheet-iron, and as soon as the yellow colour has disappeared the undissolved iron is removed, and the antimony which has come down is re-dissolved with the aid of a little ferric chloride, which is added drop by drop till the solution is distinctly yellow to ensure that all the tin is in the stannic state; a warm solution of oxalic acid containing about one third of its volume of chlorhydric acid is then added, and the antimony is precipitated as Sb_2S_3 , together with traces of sulphur, and washed with water, alcohol, and carbon bisulphide.

After the removal of the antimony the hydrogen sulphide is expelled by boiling, the oxalic acid decomposed with potassium permanganate, and the tin precipitated in a hot solution with hydrogen sulphide, and allowed to stand till cold. The SnS_2 obtained in this way can be filtered off and washed with water without passing through the filter. It is then converted, by ignition, into SnO_2 , in which form the tin is weighed. The test analyses are very satisfactory.

For qualitative purposes, in distilling off the arsenic, a condenser is not necessary, a bent tube dipping into water being sufficient. It is advisable, however, to use a safety-tube to prevent the distillate coming back.

In the case of alloys the metal is dissolved in strong chlorhydric acid with the aid of ferric chloride, and the arsenic distilled off at once. The antimony and tin, after being separated from the other metals of the group, are then estimated in the manner described above.

*2. "Platinous Chloride and its Use as a Source of Chlorine." By W. A. SHENSTONE and C. R. BECK.

The authors have examined chlorine from six specimens of platinous chloride of independent origin, and have found oxygen and hydrogen chloride to be present in them all. From these results they conclude that platinous chloride made by any of the processes hitherto recommended, including that lately suggested by L. Pigeon, contains a very perceptible quantity of some basic compound, which gives off water together with the gases previously mentioned.

They have noticed that after mercury has been exposed to the action of chlorine in the presence of a trace of water, it becomes capable of absorbing hydrogen chloride; it is not yet certain whether this action depends on the presence of oxygen or not.

*3. "Note on the Adhesion of Mercury to Glass in the Presence of Halogens." By W. A. SHENSTONE.

The author finds that carefully purified chlorine, bromine, and iodine affect mercury like ozone, causing it to adhere to glass in a remarkably perfect manner.

*4. "The Decomposition of Mannitol and Dextrose by the *Bacillus Ethaceticus*." By PERCY F. FRANKLAND, F.R.S., and JOHN S. LUMSDEN.

The products of the fermentation of both these compounds consist of ethyl alcohol, acetic acid, carbonic anhydride, hydrogen, and traces of succinic acid. When the fermentations are conducted in a closed space there is invariably also a considerable quantity of formic acid produced, whilst in fermentations in an open space (flasks plugged with cotton-wool) formic acid, except in traces, is a most exceptional product. The same phenomenon has been already pointed out by one of the authors in the case of a fermentation with another organism (*B. ethacetosuccinicus*), and it is, doubtless, due to formic acid being one of the primary products of the fermentation, and then breaking up, more or less completely, into equal volumes of carbonic anhydride and hydrogen. This decomposition is, however, retarded when the products—carbonic anhydride and hydrogen—are prevented from escaping, as is the case in fermentations conducted in a closed space. Indeed, the proportion in which the carbonic anhydride and hydrogen were found coincides almost exactly with that in which they are present in formic acid. The proportions in which the several products are obtained from mannitol is approximately represented by the equation:—

$3C_6H_{14}O_6 + H_2O = C_2H_4O_2 + 5C_2H_6O + 5CH_2O_2 + CO_2$,
whilst in the case of the dextrose the products occur in the proportions:—

$2.5C_2H_6O : 1.5C_2H_4O_2 : 3CH_2O_2 : CO_2$.

Thus, there is more acetic acid in proportion to alcohol and formic acid produced in the case of dextrose than in that of mannitol. The carbon dioxide given among the products really represents that liberated from the calcium carbonate present in excess by a fixed acid insoluble in ether, the nature of which could not be determined.

The fermentations conducted in a closed space are always found to be markedly less complete than those which take place in an open one.

There is a close qualitative and quantitative resemblance between these fermentations by the *B. ethaceticus* and those previously described by one of the authors as taking place through the agency of the *Pneumococcus* (Friedländer), which renders it probable that this ethacetic

decomposition is a very general and typical form of fermentative change.

DISCUSSION.

Dr. ARMSTRONG, after remarking on the interest attaching to the discovery of formic acid, in considerable quantity, among products of fermentation, said that he could not think the explanation satisfactory which the authors had advanced of the non-production of this acid when closed flasks were used, viz., that the breaking up of the acid into hydrogen and carbon dioxide, which took place when fermentation was conducted in open vessels, was retarded by their presence when the products were prevented from escaping: that such an influence could be exerted on a fermentation from without was scarcely probable, according to present knowledge. It was more likely that there were distinct initial differences between fermentations carried on under the two sets of conditions.

Professor FRANKLAND, in reply, said that he thought the difference might be attributable to a difference in pressure involved in collecting the gases, in the one case, over mercury, rather than to absence of air, and he was, therefore, at present studying the influence of pressure.

In reply to a question by Dr. Kipping, he added that it was very remarkable that, notwithstanding both alcohol and acetic acid were formed, no trace of ethylic acetate could be detected among the products.

*5. "The Preparation of Glycollic Acid." By H. G. COLMAN.

Glycollic acid may be readily prepared by boiling a concentrated solution of potassium chloracetate for 24–30 hours in a flask connected with a reflux apparatus. The product, which consists of a solution of glycollic acid and potassium chloride, is distilled under reduced pressure, the temperature in the distilling flask not being allowed to rise above 70°, and the residue is mixed with a large quantity of acetone, filtered from the separated potassium chloride, and the acetone solution concentrated. Glycollic acid soon separates out in colourless crystals, which only contain 0.5 per cent of ash, and are sufficiently pure for most purposes. The yield is about 85 per cent of the theoretical.

Glycollic anilide, $C_6H_5 \cdot NH \cdot CO \cdot CH_2OH$, may be prepared by heating glycollic acid for some time at 240°, boiling the residue with aniline, and re-crystallising the product from water. It has the properties assigned to it by Norton and Tscherniak (*Bull. Soc. Chim.*, xxx., 104). Attempts were made to convert this compound into oxindole—



by eliminating the elements of water, but without success. Phosphorus pentoxide acts on the anilide, but the crystalline product consists simply of the phosphate $PO(O \cdot CH_2 \cdot CO \cdot NH \cdot Ph)_3$.

According to measurements made by Mr. W. J. Pope the crystals of glycollic acid obtained from an acetone solution belong to the orthorhombic system, $a : b : c = 0.774 : 1 : 0.368$, and exhibit the macropinacoid (100), the brachypinacoid (010), the macrodome (101), and the prism (110). Glycollic acid would seem to be dimorphous, as Groth has described (*Krys. Zeit.*, v., 309), crystals of the acid obtained from aqueous solution, which belongs to the monosymmetric system. Glycollic anilide crystallises in the monosymmetric system, $a : b : c = 0.9322 : 1 : ?$; $\beta = 64^\circ 55'$, and show the orthopinacoid (100), the basal pinacoid (001), and the prism (110).

6. "Researches on Silicon Compounds and their Derivatives. Part VI. The Action of Silicon Tetrachloride on Substituted Phenylamines." By J. EMERSON REYNOLDS, D.Sc., F.R.S.

In Part V. of this investigation the author described some members of a class of silicon compounds of the type $Si(RNH)_4$, obtained by the interaction of silicon tetrabromide and tetrachloride and aniline, ortho- and para-toluidine and α - and β -naphthylamine; the action

of a silicon haloid on the secondary and tertiary alkaloids diphenylamine, ethylaniline, and diethylaniline is now described.

Diphenylamine, when free from extraneous matter capable of decomposing silicon chloride, combines with the latter to form an unstable addition compound, which is decomposed below the boiling-point of benzene. No interaction with the silicon haloid was obtained analogous to that which readily occurs with phenylamine.

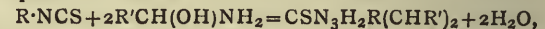
Ethylaniline, on the contrary, is easily acted on by silicon chloride, ethylaniline chlorhydride separating, a liquid product being obtained containing the new compound $Si(PhNet)_4$.

Diethylaniline, when pure, is but feebly acted on by silicon tetrachloride even when heated with it at 190° under pressure; no ethyl chloride separates, but the compound $PhNEt_2HCl$ is formed together with a liquid which probably contains the compound $Si(C_6H_5NEt_2)_4$.

It appears, therefore, that the substitution of phenyl for but one atom of hydrogen in aniline confers on the resulting alkaloid greater immunity from attack by silicon tetrachloride than displacement by ethyl of part or all the amidic hydrogen of aniline.

7. "Chemistry of the Compounds of Thiourea and Thiocarbimides with Aldehyd-Ammonia." By AUGUSTUS E. DIXON, M.D.

In a previous paper (*Chem. Soc. Trans.*, 1888, 411) the author showed that the alkyl and allied thiocarbimides and aldehyd-ammonias interact in accordance with the equation:—



and the possibility was suggested of a connection between the class of substances so formed and a compound obtained by Nencki (*Ber.*, vii., 162) by the action of thiourea on aldehyd-ammonia.

The principal general results established by a continuation of this investigation are that Nencki's compound, a homologue of the latter (obtained from thiourea and valeraldehyd-ammonia), and the thiocarbimide derivatives formed in accordance with the equation above given, agree in properties in the following respects:—

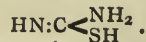
- (1) They combine with picric acid in equimolecular proportions.
- (2) They are decomposed by hot acetic anhydride, with separation of both aldehyd groups, together with one of the three nitrogen atoms, the corresponding acetylated thiourea being formed; while (3) boiling with water effects an analogous decomposition, save that the resultant thiourea is non-acetylated.
- (4) They combine with silver nitrate, forming sparingly soluble addition products, which are more or less unstable in presence of water.

From this similarity in behaviour the inference is drawn that they are members of the same class.

Though thiourea and aldehyd-ammonia readily interact this was not found to be the case when substituted thioureas were employed; under no circumstances (and the experiments were conducted under a great variety of conditions), was any sign of combination observed. This inertness is difficult of explanation if the monosubstituted thioureas possess the structure—



but is intelligible on the supposition that they are of the form—



Evidence in favour of the latter formula has already been adduced from a slightly different point of view by Prof. Emerson Reynolds (*Chem. Soc. Trans.*, 1891, 394), who, further, considers it probable that the substituting radicle displaces hydrogen in the imidic group.

The following compounds, amongst others, are described:—

Thiourea and valeraldehyd-ammonia, $\text{CSN}_3\text{H}_3(\text{C}_5\text{H}_{10})_2$ —flattened, rhombic crystals, insoluble in water, and melting between 120° and 121° (uncorr.).

Methylthiocarbimide and acetaldehyd ammonia, $\text{CSN}_3\text{H}_2\text{Me}(\text{CHCH}_3)_2$ —white needles, soluble in water and alcohol; melting-point 142° to 143° (uncorr.).

Acetylthiocarbimide and aldehyd-ammonia, $\text{CSN}_3\text{H}_2\text{Ac}(\text{CHCH}_3)_2\text{H}_2\text{O}$ —slender needles, soluble in water and alcohol; melting-point 187° (uncorr.).

Phenylcarbimide and aldehyd-ammonia, $\text{CON}_3\text{H}_2\text{Ph}(\text{CHCH}_3)_2$ —satiny needles, insoluble in water, sparingly soluble in alcohol; melting-point 199° to 200° (uncorr.).

8. "The Atomic Weight of Boron." By J. L. HOSKYN-ABRAHAM, B.A., Ph.D., late Bishop Berkeley Fellow of the Owens College. (Edited by T. Ewan and P. J. Hartog, of the Owens College.)

The deceased author determined the atomic weight of boron by estimating the amount of silver necessary to precipitate the bromine of a known weight of boron bromide. The editors have drawn up from the notes of the almost completed research a memoir which will shortly be submitted for publication. The results of the final series of determinations are as follows:

Number of bulb.	Weight of BBr_3 .	Weight of Ag.	Ratio of BBr_3 to Ag.	Atomic weight of boron ($\text{O}=16$).
19.	1.65511	2.13759	0.774288	10.838
23.	4.46783	5.77127	0.774153	10.794
25.	8.42315	10.88065	0.774146	10.792
11.	7.72194	9.97405	0.774203	10.811
32.	4.09274	5.28595	0.774268	10.831
10.	8.03235	10.37420	0.774262	10.829
Mean error = 0.017.				

The mean atomic weight is 10.816; the probable error being 0.0055.

The atomic weight obtained by taking the total of the mean weights of boron bromide and of silver used in the series of determinations is 10.811.

The atomic weights used in the calculation are $\text{Ag}=107.923$, $\text{Br}=79.951$. (Clarke, "Constants of Nature.")

It is to be noticed that an experimental error of 1 part in 1000 in the determination of the ratio of boron bromide to silver will produce an error of 23 parts in 1000 in the atomic weight, owing to the small percentage of boron present in boron bromide.

NOTICES OF BOOKS.

Laboratory Practice: A Series of Experiments on the Fundamental Principles of Chemistry. A Companion Volume to "The New Chemistry." By JOSIAH PARSONS COOKE, LL.D., Erving Professor and Director of the Chemical Laboratory, Harvard University. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1892. Small 8vo., pp. 192.

The first point which here strikes us is that this book, though printed and published in England and intended for English students—or, at least, likely to fall into their hands—contains matter intelligible only to readers conversant with American conditions. We are told that a "farina kettle" is a good steam bath, and that the "quick-sealing fruit or milk jars" are good gas-holders. But farina kettles and quick-sealing fruit-jars are not commonly to be met with on this side the Atlantic. Nor with us are balances and thermometers necessarily imported from Germany. Elsewhere we are told to "use a half-pint tincture (?) of thin glass."

We find a plate representing a kerosene stove and tube furnace, the former curiously labelled "Chemical American." Such plates are merely waste paper in a country where gas is available in every laboratory. The teachings of the book are judicious, and it might be undoubtedly recommended if it had only been remodelled in accordance with English conditions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 14, April 4, 1892.

Native Iron of the Canon Diablo.—M. Mallard.—Fragments of native iron had been discovered in March, 1891, near the Canon Diablo, in Arizona. One of these specimens was submitted to the examination of Prof. Koenig and was found extremely hard. A freshly cut surface was found interspersed with small cavities, filled with black matter and containing diamonds, one of which had a diameter of 0.5 millimetre and scratched corundum with extreme ease. The iron contained only 3 per cent of nickel; the black matter seemed to be iron carbide. In two of the cavities there were blackish grains which even scratched the cleavages of white diamond. They were probably "carbonado,"—a black diamond.

Electric Spectra of Gallium.—Lecoq de Boisbaudran.—The substance of this memoir consists of tabular views of the rays obtained. The author remarks, in conclusion: "We see what curious changes the spectrum of gallium undergoes if the nature of the spark is caused to vary. As analogous changes are produced in a more or less remarkable manner with almost all substances it is very necessary to define the conditions under which electric spectra have been obtained."

The Production in the Dry Way of Some Anhydrous Crystalline Sulphates.—P. Klobb.—The substances thus obtained are zinc sulphate, anhydrous copper, cobalt and nickel sulphates.

Nitroketone derived from the Camphosulphophenols.—J. Cazeneuve.—The two isomers, amethylcamphophenolsulphone and amethylcamphophenolsulphonic acid, undergo a remarkable transformation. The sulphur connected to the nucleus resists concentrated hydrochloric acid and boiling potassa-lye, but in contact with nitric acid it is set free in the state of sulphuric acid whilst the group NO_2 is substituted. The mol. also loses 2H in the state of water.

On the Composition of Pinnaglobine.—a Novel Globuline.—Dr. A. B. Griffiths.—Already inserted.

Journal für Praktische Chemie.
Vol. xliv., Nos. 21 and 22.

Researches from the Laboratory of A. Weddige.—These comprise a very extensive memoir on the action of sulphonic acid chlorides upon orthoamidabenzamide by Ernst Franke.

Researches from the Laboratory of the University of Freiberg.—Here are included a paper by Ad. Claus and Howitz on the action of bromine upon para- and oxyquinoline; a memoir by C. Willgerodt and E. G. Mühe on picrylic, orthoparadinitrophenylic, and nitroazo- or nitronitrosoazometachlorophenylhydrazine and their derivatives, including a tabular view of the formulæ, colours, forms, melting-points, decomposition points, and

solubilities in water, alcohol, glacial acetic acid, benzene, ether, and chloroform, of 26 compounds, and a paper on paranthracen by Karl Elbs, in which the author states that derivatives of paranthracen have not yet been obtained by means of any reagent.

On a Method for Determining the Constitution of Saturated and Non-Saturated Haloid Derivatives and Hydrocarbons.—Mejer Wildermann.—This paper does not admit of useful abridgment.

Action of Oxidising Agents upon Aliphatic Thioureas.—D. S. Hector.—In two earlier papers the author has published in the *Berichte* (xxii., p. 1176, and xxiii., p. 357) his researches on the behaviour of the aromatic substituted thioureas with oxidising agents, especially with a three per cent solution of hydrogen peroxide. He now extends these investigations to certain thioureas of the aliphatic series, and to allylic-methylic and to simple thiourea. The reaction which occurs on the oxidation of the aromatic thioureas with hydrogen peroxide in an acid solution takes place also when aliphatic thioureas are treated with the same oxidising under the same conditions, but it is completed only to the extent of one half.

On Two New Selenious Salts.—R. Schneider.—The salts are the potassium seleno-stannate and the corresponding sodium salt.

An Explanation.—Ad. Claus.—The author declines to continue the controversy with Herr Michael as devoid of interest.

Bulletin de la Société Chimique de Paris.
Parts vii. and viii., No. 5, March 5, 1892.

Determination of the Congelation-Point of very Dilute Aqueous Solutions. Application to Cane-Sugar.—F. M. Raoult.—The author has determined the lowering the freezing-points of solutions of cane-sugar, taking in preference the most highly diluted.

Separation and the Determination of Lead, Silver, and Zinc, in Ores composed of Galena and Blende.—Emile Aubin.—Already noticed.

Action of Propyl Iodide upon Pure Trimethylamine in Aqueous Solution, and in Equimolecular Proportions in the Cold. Trimethylpropylammonium Iodide.—H. and A. Malbot.—This process is much more rapid than that of isoamyl iodide, and especially than that of isobutyl iodide. In 18 hours the ether has almost completely disappeared.

Action of Isopropyl Iodides upon Pure Trimethylamine in Aqueous Solution, and in Equimolecular Proportion in the Cold and at 100°. Trimethylisopropylammonium Iodide.—H. and A. Malbot.—The action of heat does not interfere with the normal reaction, as it occurs in the cold. In each case the result is the entire conversion of the isopropyl iodide and of the trimethylamine into trimethylisopropylammonium.

Action of Allyl Iodide upon Pure Trimethylamine in Aqueous Solution and in Equimolecular Proportion. Trimethylallylammonium Iodide.—H. and A. Malbot.—If trimethylamine is allowed to fall drop by drop into allyl iodide it occasions slight explosions, as does bromine.

The Rotatory Power in Silks of Different Origins.—Leo Vignon.—The author has already shown that silks if examined in certain solvents exert a considerable rotatory power upon polarised light. He applies the differences to a determination of different kinds of silk.

Revue Universelle des Mines et de la Metallurgie.
Vol. xvii., No. 2.

This issue does not contain any chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, May 2nd.—Medical, 8.30. (Annual Oration).
Society of Chemical Industry, 8. "The Distillation of Wood," by Prof. W. Ramsay, F.R.S., and J. C. Chorley. "Notes on the Composition of some Indian Gums of Known Origin," by Dr. S. Rideal.
— Royal Institution, 5. (Annual Meeting).
— Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Theories," by Percy F. Frankland, F.R.S. (Cantor Lectures).
TUESDAY, 3rd.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "The Sculpturing of Britain—its Later Stages," by Prof. T. G. Bonney, D.Sc., F.R.S.
— Pathological, 8.30.
WEDNESDAY, 4th.—Society of Arts, 8. "The Bradford Corporation Electricity Supply," by W. H. Preece, F.R.S.
THURSDAY, 5th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Chemistry of Gases," by Prof. Dewar, F.R.S.
— Chemical, 8. Ballot for the Election of Fellows.
FRIDAY, 6th.—Royal Institution, 9. "The Sensitiveness of the Eye to Light and Colour," by Capt. Abney, F.R.S.
— Geologists' Association, 8.
— Quekett Club, 8.
SATURDAY, 7th.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Dannreuther.

ERRATA.—P. 203, foot of col. 2, the formula for pinnaaglobine should read $C_{724}H_{985}N_{183}MnS_4O_{210}$, and for "NO₂" read "NO."

NEW PUBLICATIONS.

THE TANNINS; a Monograph on the History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents, with an Index to the Literature of the subject. By HENRY TRIMBLE, Ph.M. Vol. I., crown 8vo., cloth. 10s. 6d.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1693.

PRELIMINARY NOTE ON THE YELLOW CRUSTS OF THE FUMAROLE IN THE CRATER OF VESUVIUS, AND THE NEW METAL VESBIUM.

By DR. T. L. PHIPSON,

Graduate of the Faculties of Science and Medicine of the University
of Brussels, Fellow of the Chemical Societies of London, Paris,
Antwerp, &c.

FORMERLY I discovered notable quantities of selenium in the arseniferous sulphur of Puzzuoli, near Naples (1862). I have lately examined the lava and yellow crusts of the fumarole from the crater of Vesuvius (specimens taken in 1879), and have found, besides the substances usually met with in volcanic products, considerable quantities of fluorine, which appears to have escaped the notice of Sylvestri, and minute quantities of molybdenum, which has perhaps given rise to the belief that a new metal, vesbium, exists in the yellow and green crusts of some ancient lava of Vesuvius, as described by the veteran observer A. Scacchi.

I have also found notable quantities of fluorine in the black lava (with white grains of leucite) of 1864; and it will probably be found that fluoride of silicium escapes with the dense white steam which issues from these apertures.

Since my distinguished friend, the late Prof. Nicklès, of the Faculty of Science of Nancy, showed that concentrated sulphuric acid, heated with rocks supposed to contain fluorine, would attack and corrode plates of glass when no fluorine was present, and that to make use of this familiar test it is absolutely necessary to use plates of polished quartz, and, moreover, since fluorine will escape in these circumstances from siliceous minerals in the form of fluoride of silicium which does not immediately attack either glass or quartz, I have had to find some method which would give accurate results and avoid the use of quartz plates, which are expensive. I have got over the difficulty thus:—To a few grms. of the pulverised rock in a very small glass beaker concentrated sulphuric acid is added, and the beaker covered with a clean glass plate. Another beaker exactly similar containing the same quantity of sulphuric acid, but no rock, and covered with a similar glass plate, is placed alongside as a witness, and the two are left thus at the ordinary temperature of the laboratory for the space of three days. At the end of that time the glass plate over the fluoriferous rock will be found corroded, whilst the other remains quite bright. This interval is necessary when fluo-silicic gas is chiefly evolved; with minerals containing little silica the test can be made in a few hours.

The exact nature of the yellow crust of the fumarole has proved a puzzle to many an acute observer. The guides sometimes present visitors with fragments of the cellular lava covered with this crust as specimens of "sulphur" (sublimates of sulphur at Vesuvius are rare), and I know one case in which a lady packed some of these so-called "sulphur" specimens into a box containing a favourite silk dress, which was soon destroyed. These yellow crusts are highly deliquescent and acid; they are impregnated with acid chlorides and sulphates of iron, aluminium, calcium, sodium, &c. The Italian coarse grey paper in which the specimens were enveloped was so thoroughly impregnated with these acid salts that, after being thoroughly dried, it was quite incombustible.

It was to "perchloride of iron" that Prof. Scacchi at first felt inclined to attribute the yellow colour of these

incrustations; but when he found that this colour resisted the action of water he hesitated; and after a considerable number of ingenious tests, he came to the conclusion that it was due to "a very complicated mixture of various substances." He did not succeed in establishing the precise nature of the yellow substance to which the crusts owe their colour (*Sul'incendio Vesuviano, &c.*, 1855).

I have found that the lava covered with this yellow incrustation when mixed with boiling water rendered the latter very acid, and that pure water extracted a large amount of saline matter: chlorides and sulphates of iron, aluminium, alkaline earths, and alkalis; substances due to the action of hot steam with hydrochloric and sulphurous acids (and probably hydrofluoric acid, as we shall see), on the constituents of the rock. The temperature at which this vapour issues is 120° to 200° C., and sometimes much higher (500° C. has been noted in some cases).

Treated with strong sulphuric acid in the manner above described the incrustations gave abundant evidence of fluorine. That the yellow sulphur colour was not entirely due to any basic chlorides or sulphates of iron was proved when I submitted the yellow substance to the action of hot hydrochloric acid. It appears largely due to a silicate of peroxide of iron, associated with more or less fluo-silicate, and only partially attacked by acids.

A silicate of iron with very similar characters, except that it is hydrated and soluble in hydrochloric acid, is found in Mexico, and has been called Anthosiderite, from *Anthos*, a flower, because it is often seen in the form of flower-like incrustations. It is curious to note that Scacchi has also met with the yellow incrustations at Vesuvius in the form of flowery crystallisations (*floritura*, as he calls them). My specimens showed in some cases minute radiating crystals, but nothing like flower petals or feathers.

The pulverised substance, after the action of hydrochloric acid, I found to be still of a light yellow tint, and examined under the microscope the grains of transparent felspar (ryacolite) were seen to be stained, like a yellow topaz, to the extent of a quarter to a half or more of their substance by the yellow compound. This shows, over again, how porous are the most solid rocks and even crystals! The incrustations have a strong odour of fluo-silicic gas, and it was this odour that led me to seek for fluorine in them.

With regard to the metal Vesbium, after carefully reading the paper of Prof. Scacchi (*Atti. della R. Acad. Napoli*, viii., 10), I am almost convinced that he was dealing with molybdenum and copper (and probably minute quantities of other substances), in the green and yellow crusts which he examined on the ancient Vesuvian lava. Nevertheless, further research is requisite, and I hope to repeat his experiments on the incrustated lava still in my possession.

The manner in which I detected molybdenum in the yellow crusts from the fumarole found in the crater of Vesuvius in the Spring of 1879, is as follows:—

The finely pulverised lava and its incrustation is treated with hot *aqua regia*; the solution, slightly evaporated and without filtering, is neutralised by ammonia in slight excess; yellow sulphide of ammonium is added, and the mixture allowed to remain for some hours in a closed vessel. It is then rapidly filtered and the filtrate neutralised with hydrochloric acid in slight excess. The flask is closed immediately with a cork, and allowed to remain thus for two days. At the end of that time the brown sulphide of molybdenum will be found upon the precipitated sulphur. (The sulphide of molybdenum requires a long time to precipitate in an acid liquid, and more so when its quantity is small). The precipitate is collected on a platinum dish and roasted, to drive off the sulphur and convert the sulphide into molybdic acid.

Copper and lead are invariably present in small quantities in the incrustated cellular lava. The yellow crust also yields ammonia, and there are indications of many

other substances to which I may refer later. I find that the lava after being treated with a boiling solution of caustic soda, *gelatinises* with hydrochloric acid, and this character may, perhaps, enable us to distinguish between the lava of modern and of ancient volcanoes.

Laboratory of Analytical Chemistry,
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RESEARCHES ON TURACIN, AN ANIMAL PIGMENT CONTAINING COPPER.*

PART II.

By A. H. CHURCH, M.A., F.R.S.,

Professor of Chemistry in the Royal Academy of Arts, London.

THIS paper is in continuation of one read before the Society in May, 1869 (*Phil. Trans.*, cliv, pp. 627—636). It contains an account of observations made by other investigators on turacin and on the occurrence of copper in animals; a table of the geographical distribution of the Touracos, and a list of the twenty-five known species; a chart of turacin spectra (for which the author is indebted to the kindness of Dr. MacMunn); and a further examination of the chemical characters and the composition of turacin. The more important positions established by the present inquiry are these:—

1. The constant occurrence in eighteen out of the twenty-five known species of *Musophagidae*, of a definite organic pigment containing, as an essential constituent, about 7 per cent of copper.

2. The "turacin-bearers" comprise all the known species of the three genera, *Turacus*, *Gallirex*, and *Musophaga*, while from all the species of the three remaining genera of the family *Musophagidae*, namely, *Corythaola*, *Schizorhis*, and *Gymnoschizorhis*, turacin is absent. Furthermore, the zoological arrangement of the genera constituting this family is in accord with that founded on the presence of turacin.

3. The spectrum of turacin in alkaline solution shows, besides the two dark absorption bands previously figured, a faint broad band on either side of line F, and extending from $\lambda 496$ to $\lambda 475$.

4. The spectrum of *isolated* turacin in ammoniacal solution shows, besides the three bands already named, a narrow fourth band, lying on the less-refrangible side of line D, and extending from $\lambda 605$ to $\lambda 589$. It probably arises from the presence of traces of the green alteration product of turacin formed during the preparation of that pigment in the isolated condition; an alteration product which is likely to prove identical with Krukenberg's turacoverdin.

5. Turacin in ammoniacal solution remains unchanged after the lapse of twenty-three years.

6. Turacin in the dry state, when suddenly and strongly heated, yields a volatile copper containing red derivative, which, though undissolved by weak ammonia-water, is not only soluble in, but may be crystallised from, ether.

7. Turacin in the dry state, when heated in a tube surrounded by the vapour of boiling mercury, becomes black, gives off no visible vapour, is rendered insoluble in alkaline liquids, and is so profoundly changed that it evolves no visible vapour when afterwards strongly heated.

8. The accurate analysis of turacin offers great difficulty. The percentage composition, as deduced from those determinations which seem most trustworthy, is—

Carbon	53.69
Hydrogen	4.60
Copper	7.01
Nitrogen	6.96
Oxygen	27.74

These numbers correspond closely with those demanded by the empirical formula $C_{82}H_{81}Cu_2N_9O_{32}$, although the author lays no stress upon this expression.

9. Turacin presents some analogies with hæmatin, and yields, by solution in oil of vitriol, a coloured derivative, turacoporphyrin. The spectra of this derivative, both in acid and alkaline solution, present striking resemblances to those of hæmatoporphyrin, the corresponding derivative of hæmatin. But copper is present in the derivative of turacin, while iron is absent from its supposed analogue, the derivative of hæmatin.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING MARCH 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, April 19th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 186 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 186 samples examined, the whole were found to be clear, bright, and well filtered.

The satisfactory character of the water supply to the Metropolis, commented on in our previous report, continued to be maintained during the month of March, the figures indicative generally of the smallness of the proportion of organic matter present in the water being substantially identical, though just a trifle higher, than those afforded by the results of the previous month, as shown in the following Table, in respect to the water furnished by the several companies drawing their supply from the Thames:—

	Ratio of brown to blue tint.	Oxygen re- quired for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
January	12.4 : 20	0.052	0.158	0.204
February	8.3 : 20	0.039	0.137	0.151
March..	8.6 : 20	0.043	0.144	0.188

We cannot close this report without giving expression to our sense of the loss we have sustained by the premature death of our much valued colleague, Dr. Meymott Tidy, esteemed not only by ourselves, but by all with whom he was brought into relationship, alike for his great professional knowledge and experience, especially in regard to water analysis and supply, and for his bright, kindly disposition and high personal character.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

AN EPISODE IN THE HISTORY OF SCIENCE.

AN incident which has been recently brought to light is not uninteresting. Close upon half a century ago, Mr. J. J. Waterston submitted to the Royal Society a memoir on "The Physics of Media composed of Free and Perfectly Elastic Molecules in a State of Motion." In accordance with routine, it was submitted to experts supposed to be qualified to form a just estimate of its merits. One of these referees pronounced the opinion that "the paper is nothing but nonsense, unfit, even, for reading before the Society." Another expert, who was also one of the leading authorities of the day, and who had evidently given the memoir his best attention, announces that: "The original principle itself involves an assumption which seems to me very difficult to admit, and by no means a satisfactory basis for a mathematical theory, viz., that the elasticity of a medium is to be measured by supposing its molecules in vertical motion and making a succession of impacts against an elastic gravitating plane." In consequence, Waterston's memoir was indeed read, and a brief and somewhat perfunctory abstract was printed in the *Proceedings*, but since then it has lain practically unnoticed in the archives of the Society. An account of the paper appeared also in the "Report of the British Association" for 1851.

So matters remained. Other persons arrived at conclusions similar to those announced by Waterston, and in due time reaped the credit of so doing. But, at last, Lord Rayleigh, Secretary to the Royal Society, unearthed Waterston's memoir, and has been instrumental in securing its appearance in the *Philosophical Transactions*.

It must not be supposed that we are taking up here our parable either against the Royal Society as a body or against the men upon whose judgment it relied. Scientific bodies with a high and well-earned reputation have to be very cautious to what papers they give their *imprimatur*. The referees also could judge only according to their own lights, and may in turn demand to be judged accordingly.

Lord Rayleigh makes here two suggestions which may be of use for the future. He thinks that "highly speculative investigations, especially if by an unknown author, are best brought before the world through some other channel than a scientific society." He even intimates that a young author who feels himself capable of great things might do well, before attempting higher flights, to perform work of a more limited scope and more easy to be appreciated. Did not Charles Darwin pursue this plan when he produced his monographs on Coral Reefs and on the Cirripedia? and was thus enabled to pose before the world as a sound and sober-minded inquirer before he dazzled his contemporaries with the startling search-lights of the "Origin of Species."

Another lesson implied in Lord Rayleigh's introduction to Waterston's paper, is conveyed in the following remark:—"One circumstance which may have told unfavourably upon the reception of Waterston's paper is that he mentions no predecessors." A young or a comparatively unknown inquirer will always find it good policy, if possible, to put forward his results or his conclusions as a development of what has previously been done in the same direction. Such a step, if judiciously taken, will guarantee the innovator against contemptuous disregard, as well as against an intentional "conspiracy of silence."

The value of Waterston's paper is now, of course, mainly historical. The work which he began has since been taken up and carried out by others. It must be admitted that Waterston first introduced the conception that heat and temperature must be measured by *vis viva*. Thus he completed Bernoulli's explanation of pressure by showing the accordance of his hypothetical elastic medium with the law of Dalton and Gay-Lussac. In the

second section of his paper, Waterston showed that "in mixed media the mean square molecular velocity is inversely proportional to the specific weight of the molecules." From this generalisation, the law of Avogadro, and that of Graham on diffusion, may, as Lord Rayleigh reminds us, be deduced at once.

The chemical views advanced in his paper, in the opinion of Professor McLeod, "shadow forth many of the ideas of modern chemistry, and it might have been the means of hastening their reception by chemists."

Waterston distinctly expresses the opinion that "a molecule in motion, without any face to restrain or qualify it, is in every respect to be considered as a free projectile. Allow such free projectiles to be endowed with perfect elasticity, and likewise extend the same property to the elementary parts of all bodies that they strike against, and we immediately introduce the principle of the conservation of *vis viva* to regulate the general effects of their fortuitous encounters." Here, surely, the author approached very close to our modern kinetic theory of gases.

RESEARCHES ON THE METALS OF THE CERIU GROUP.*

TREATISE I.

By P. SCHÖTTLANDER:

(Continued from p. 206).

WE dissolve in 10 to 20 parts of hot water crystalline oxalic acid to the extent of $1\frac{1}{2}$ parts of the quantity of oxide existing in solution, and add a small portion of the hot solution strongly acidulated with nitric or hydrochloric acid, and extremely diluted at first (containing about one-half per cent of oxide). The oxides separate at once as a semi-fluid mass, which generally collects together in soft lumps. These must not be immediately pressed with the glass stirring-rod, but the operator must wait for a few minutes until the oxalates have passed into a solid state, when the masses are broken up and the liquid is stirred briskly, when the precipitate in general distributes itself in the liquid for the most part as a fine powder; a further portion of a hot and rather more concentrated solution is added, again proceeding as just directed, until the liquid contains a considerable quantity of a fine powder.

The residue of the hot acid solution containing about 3 per cent of oxides is then added at once, stirring vigorously. The very voluminous precipitate is washed by decantation, allowed to drain on a filter, dried at 100° until it begins to crumble, and then completely dried over an open flame. A previous extraction of moisture is not advisable, as the mass forms then too compact fragments. The ignition of the oxalates in large quantities may, without hesitation, be undertaken in an iron capsule with a flat bottom. This vessel must have been previously scoured with sand, dried, rubbed with olive oil, and then heated to incipient redness. The iron thus becomes coated with a firmly adhering layer of ferrous-ferri oxide, which does not exfoliate even on repeated use.

When igniting the oxalates the following precautions must be carefully observed:—If after the destruction of the oxalic acid and the combustion of the carbon the oxide does not form a quite fine powder, but contains solid fragments, it must be allowed to cool, then be ground up finely in a mortar and ignited anew. During ignition the mass is diligently turned over and over so that all parts of the powder which have assumed a red heat on the bottom of the capsule may be brought in contact with the air whilst at this temperature. Thus the oxides are obtained as a fine uniform powder of a dark chocolate-brown colour. An oxide containing particles which have retained a light colour is not fit for the subsequent operation.

* *Berichte der Deutsch. Chem. Gesell.*

For separating cerium and freeing the basic cerium precipitate as far as possible from lanthanum and didymium, the proportion of nitric acid prescribed by Auer is not quite sufficient (supposing acid of 1.40 spec. gravity is understood) if lanthanum and didymium are present in percentage here assumed. It is most satisfactory to ascertain the requisite quantity of nitric acid by some previous experiments with small quantities of oxide. To this end 30 grms. oxide are stirred up with 30 c.c. of water in a porcelain capsule to a uniform paste, and at first 60 grms. nitric acid are added of specific gravity 1.20. On stirring, the mixture becomes heated, and a part of the oxide, including much cerium, dissolves with a yellow colour and with an escape of gas. The capsule is then heated on the water-bath for an hour, stirring diligently and supplying the water lost by evaporation. At the end of this time all the undissolved oxide is opened up, and the dissolved cerium is separated again. If small clots appear they are crushed with the pestle. So much water is then added that the total weight of the mixture reaches 140 grms., and it is then heated for an hour on the water-bath, with frequent stirring. If the liquid is now of a rose colour and the precipitate of a yellowish white, the quantity of nitric acid is sufficient. If the precipitate, on the contrary, is of a brownish rose colour, the liquid is evaporated down to the volume which it had before the addition of the nitric acid, and there are cautiously added from time to time whilst heating small portions of nitric acid of specific gravity 1.20 from a weighed flask, until the precipitate, after dilution to a total weight of 140 grms. and heating, has assumed a white or yellowish white colour. If the liquid as it becomes clear on the surface has a yellow instead of a rose colour, too much nitric acid has been added, and cerium has again passed into solution. In this case the dissolved cerium may be entirely re-precipitated by heating with a little oxide ground up with water in a mortar. After the sample has stood for twelve hours, a few drops of the solution are filtered through a dry filter, and the absence of cerium is ascertained by the extremely sensitive reaction with hydrogen peroxide, indicated by Lecoq de Boisbaudran. The same reagent was previously used by W. N. Hartley for the recognition of cerium, though in a somewhat different manner. The clear filtrate is best mixed, first with solution of hydrogen peroxide, then with a little strongly diluted ammonia until a turbidity begins to appear, and is then heated. In presence of cerium the gelatinous precipitate has an intense orange-yellow colour, whilst salts of lanthanum and didymium give only a colourless or a pale rose-coloured precipitate.

For the separation of the cerium, 500 grms. of the tested oxides are stirred up to a uniform paste with 200 c.c. of water in a capacious semicircular porcelain dish, and nitric acid of specific gravity 1.20 is slowly added in the proportion already ascertained, with stirring. In general, from 1100 to 1350 grms. of such acid will be required. After the violent reaction is over, the dish is placed upon a water-bath, kept in gentle ebullition, and heated for several hours, stirring frequently and occasionally replacing the water which has evaporated, until all brownish particles of oxide have been converted into yellowish white masses. The mass is then allowed to stand for nine hours, mixed in a decantation glass with $2\frac{1}{2}$ litres of cold water, and allowed to settle for twenty-four hours.

The rose-coloured solution (which contains not a trace of cerium if the operation has been properly conducted) is poured off as clear as possible, and the liquid, which is turbid from a small quantity of precipitate, is poured into another vessel. The latter liquid is then poured upon a dry filter, and the filtrate is returned and re-filtered until perfectly clear. The solution which was first decanted off is then passed through the same filter.

The precipitate is now stirred up with $2\frac{1}{2}$ litre solution of ammonium nitrate containing 7 per cent of the salt, again allowed to subside, and the liquid decanted off is poured upon a fresh filter moistened with the solution of

ammonium nitrate, and proceeding as above in case the filtrate is turbid. The clear filtrate containing ammonium nitrate is collected separately. The precipitate may then be washed a second time in the same manner, though this is generally not worth the trouble. The precipitate is best brought upon the filter last used and allowed to drain completely with cautious stirring, when almost the entire quantity may be removed from the filter as a tough clayey mass.

The precipitate, dried at 100°, is then worked up for the pure cerium double salt as directed in the former section.

This remarkable substance possesses very different properties, and in any case different compositions, according to its manner of preparation. If it was separated from a mixture of oxides very rich in cerium it is, as Auer found, soluble in pure water, and from this solution it may be again precipitated by dilute nitric acid or ammonium nitrate, whilst the oxide obtained from an oxide containing the proportion of cerium above supposed is quite insoluble in pure water. In general, the precipitate dries up to a yellowish white powder, but if so much nitric acid was used in its preparation that a little cerium was dissolved, it appears, when dry, as a transparent mass resembling amber.

It is probable that in this substance there are not merely different ceric sub-nitrates, but also cerous oxide. By the method described, and by repeatedly working up the cerium double salt, there were obtained 808 grms. earths absolutely free from cerium, consisting of about one-half lanthanic oxide along with oxides of the didymium components.

(To be continued).

APPARATUS FOR THE DELINEATION OF CURVED SURFACES, IN ILLUSTRATION OF THE PROPERTIES OF GASES, &c.

By MORRIS LOEB, Ph.D.

In attempting the graphic representation of the relations between the volume, temperature, and pressure of gases, or of other problems involving three variables, one is met by the difficulty of properly constructing the surfaces in question. Drawing isothermals, &c., as projected upon a single plane, gives a very imperfect idea of the actual proportions. For many years this method has been occasionally supplanted by the actual construction, in papier maché or plaster, of models bounded on one side by the surface in question, relief maps in other words. This plan suffers from several disadvantages. Aside from the notion of solid volume which is involuntarily entertained in beholding such a model, some of the surfaces are too complex to be well shown in this manner. Furthermore, the models are rather hard to make, expensive, and occupy a good deal of room.

I have obviated most of these difficulties by obtaining a set of glass plates, about 11 c.m. square and 7 m.m. thick, ruled in squares 7 m.m. wide. Placed one on top of the other, these form a block whose perpendicular edge may be taken for the third axis in a system of rectangular co-ordinates. Having drawn upon a sheet of paper the curves representing the relation between volume and pressure at successively 0°, 10°, 20°, 30°, &c., of temperature, I can trace them, with suitable grease-chalks, upon the successive glass plates. When these are superposed, the curves exhibit the proper relations in space and afford a very fair idea of the nature of the surface of which they are elements, without arousing any sensation of an included volume. Since the lines can always be erased and replaced by others, a set of twenty plates suffices for all purposes, and the surfaces can be produced at a moment's notice if the necessary sketches on paper are preserved. Besides being useful for illustrating lectures in molecular

physics, the plates can also be employed to advantage in the construction of crystallographic, geological, and other models.

Where the parallax, inevitable for glass plates, becomes annoying, it is possible to substitute wide-meshed cotton netting, stretched upon square frames of uniform thickness. The curves can be embroidered upon the net, as it were, with pieces of coloured thread; although it is not quite so easy to make the lines conform to the drawing, the general effect remains the same.—*Journal of the American Chemical Society*, xiii., No. 10.

NOTE ON A QUALITATIVE TEST FOR CHROMIUM.

By L. W. McCAY, D.Sc.

In most works on qualitative analysis it is directed that an insoluble chromate* or a mixture of ferric, aluminic, and chromic oxides be tested for chromium by fusing the chromate or mixture with sodium carbonate and nitrate, treating the fused mass with water, filtering, and adding acid to the yellow filtrate. This addition of acid is said to change the yellow colour of the filtrate to a reddish yellow—changing the neutral salt to an acid salt. This would, of course, be true were there after the fusion no reducing agent present in the melted mass. There is, however, formed during the fusion a considerable quantity of alkali nitrite which dissolves with the chromate and which, upon the addition of acid to the filtrate from the insoluble residue, splits up into a corresponding alkali salt and free nitrous acid. This nitrous acid is often present in such quantities as to almost immediately (especially when the liquid is heated) reduce all the chromic acid to chromic oxide, and occasion a greyish blue solution, which can completely mislead the beginner. I venture to call attention to this point, which I insist is of sufficient significance to warrant mention, at least in such a standard work as that of Fresenius. It is but proper to add that in the "Quantitative Analysis" of both Rose and Fresenius the reducing action of the nitrous acid is mentioned, but, in Rose, with what seems to me scarcely a sufficient amount of prominence.

DIFFERENCES IN THE DETERMINATION OF REVERTED PHOSPHORIC ACID BY THE OFFICIAL METHOD OF ANALYSIS.†

By CHARLES GIBSON.

(Concluded from p. 210).

Now, I am of the opinion that a critical examination of the ammonia citrate solutions of the majority of State and analytical chemists would reveal the fact that they are very close in composition to my solution A—in fact, slightly inclined to acidity, the fact of slight acidity in the solution affecting the insolubility of the aluminic phosphate not being generally known; while the chemists of the manufacturers, and perhaps a few others, being cognisant of this fact, have taken precautions to have their solutions incline to alkalinity rather than acidity. In some such way as this may we account for a considerable portion at least of the large difference in the amounts of available P_2O_5 found by Messrs. Stillwell and Gladding on the one hand, and the State chemists and myself on

the other. The results obtained in these experiments, which are only a few out of many that I have made, warrant, I think, the following conclusions:—

(1). That the official method, as it stands at present, is incapable of giving results on which an equitable adjustment of values—especially of aluminic phosphates—can be made, and it is urgently and imperatively necessary that either such modifications be made in it as will assure accuracy in all instances and under all circumstances, or that it be abandoned in favour of some other that may be depended upon.

(2). That it is possible to make such modifications in it as will enable analysts to obtain uniform and concordant results.

(3). That these modifications, if made in the direction which I will suggest, would conduce to greater accuracy and uniformity of results in the analysis of calcium phosphates.

With the view of making the comparison with the alkaline citrate method as accurate as possible, the amounts of available P_2O_5 obtained by it in these experiments and here given were determined as pyro-magnesium phosphate, checks being made by duplicates determined volumetrically. The agreement between the pyro-magnesium and volumetric determinations was very close, never varying more than 0.07 per cent. I have largely used this method during the last seven or eight years, and I have found it much more satisfactory than any other. The results obtained by it are reliable and uniform. It does not require that nicety and delicacy of manipulation and adjustment of solution that the official and other methods require, and there is therefore less liability to error. It is more expeditious, the available being determined in one operation. The presence of organic matter does not impair the accuracy of the results either for total or available P_2O_5 , and it is therefore unnecessary to destroy it. The results can be obtained either gravimetrically or volumetrically. The only drawback I find in the use of the method is that, in order to make sure of a complete precipitation of the ammonia magnesia phosphate, after adding magnesium mixture and vigorously agitating it, I find it necessary to let it stand over night. As a substitute for the present official method, if the Association decides to abandon it, I think it might go farther and fare worse; and in any case it ought to be made an alternate method.

The present official method has been clearly demonstrated to be defective, erroneous, deceiving, and the cause of great financial loss in one case at least; and this Association, with whom alone rests the responsibility, and to whom alone we must look for a remedy, will, I am sure, recognise the necessity, and make some immediate change that will not only restore confidence, but will conduce to uniformity and constancy of results, and insure accuracy and justice.

I am aware that capricious changes in official methods of analysis are to be deprecated, but in view of the facts here presented, I realise that this association must perforce take action in the premises. Therefore, with a full consideration of all the facts, and the conclusions fairly deducible from these experiments, and with a desire to aid the Association in solving the problem with which it is now brought face to face, firmly believing that the changes here advocated will be a full and complete remedy for the defects in the official method which have been brought to light, I most respectfully submit the following suggestions:—

(1). That instructions be given to add ammonia hydrate to the ammonia citrate solution, until a faint alkalinity is perceptible with red litmus paper.

(2). That the time of digesting be made one hour at 65° C.

(3). That Joulie's alkaline citrate method, with or without the modification of weighing as pyro-magnesium phosphate, be made an alternate method.

* "Fresenius's Qualitative Analyse," Vierzehnte Auflage, §138, 10. Under Chromic Oxide, however, §102, 8, he says that potassium chlorate serves the purpose better than the nitrate. No reason for this substitution is given.

† From the *Proceedings* of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

NOTES ON IRON IN BONE-BLACK.*

By Dr. BRUNO TERNE.

THE freshly-prepared bone-black of the market yields on an average from 0.1 to 0.3 per cent of iron in the form of metallic iron, originating principally from iron mixed with the bones gathered up by the junk dealers, another portion coming from the wear and tear of the bone crushers and mills, and a very little from the iron vessels used in burning the bones.

Having been in charge for the last fifteen years of one of the largest plants for manufacturing bone-black, I had never experienced any trouble with our product, on account of the iron, until several months ago, when one of our patrons complained of an excess of iron in our black, which, according to his investigation, had run up in one instance to one-half of one per cent.

This complaint was coupled with the assertion that an increase of 0.25 per cent of iron above the average would materially impair the process of refining sugar.

This charge coming from a source commanding serious consideration, caused us to look into this matter thoroughly, but an examination of the literature of sugar refining, covering a period commencing with 1872 (Wagner's *Fahrvesberichte*) up to date, failed to disclose a single case in corroboration of the above cited assertion.

The more I thought over the matter the more I became convinced that the complaint made against our black, that it impaired the work of refining sugar liquors, was merely a convenient pretext to shield some irregularities in the process of refining, which otherwise would have to be shouldered at home. We all know that organic acids will dissolve iron, but in refining sugars the liquors should be free from acids, or, at least, nearly made free by previous neutralisation; the traces of free organic acids must certainly all be absorbed by the 6 to 7 per cent of carbonate of lime contained in fresh bone-black. The fact that in discarded black the yield of carbonate of lime is reduced to 3 or 4 per cent, and the yield of iron considerably raised, demonstrates clearly that fresh black operates to free sugar liquors from iron as well as other impurities.

In order to ascertain what effect a solution acidified with organic acid would have on the iron in bone-black, I prepared two solutions of citric acid containing respectively 0.1 per cent and 0.25 per cent of free acid.

The acidity of these solutions is so great that no sugar liquor entering filters will ever approach it in acidity.

I selected a black which had given by analysis a yield of 0.5 per cent of iron, and made the following experiments:—

Grms.	C.c.	Per cent.
(a). 5 of black with 500 citric acid solution of . .		0.1
(b). 10 " " " " "		0.1
(c). 5 " " " " "		0.25
(d). 10 " " " " "		0.25

I exposed the four flasks on the top of a steam heater for twenty-four hours to a temperature of 150° to 160° F., after which I tested the still acid solution for iron with potassium sulphocyanide and potassium ferridcyanide, but no trace of iron could be found in the solution.

Not satisfied with this I kept the flask for eighteen hours on a steam bath at a temperature of 200° to 212° F.; the results of the two experiments were absolutely the same.

To operate on a sample of black large enough to place the result of the experiment beyond any doubt, I took 250 grms. of the same black, yielding $\frac{1}{2}$ per cent of iron, and treated the same with two litres of citric acid solution containing 0.25 per cent free citric acid, for twenty-four hours on the steam bath at nearly 212° F.

At the end of this time the acidity of the solution had

completely disappeared and the absolutely neutral solution showed not a trace of iron with the most sensitive reagents (potassium sulphocyanide and potassium ferridcyanide).

I went still a step further and prepared a solution of iron in citric acid, 200 c.c. of which contained 1.01 grms. of iron; I took 100 c.c. and diluted to 500 c.c.; I mixed the dark yellow solution in a flask with 500 grms. of fresh regular sugar-house black, boiled up for thirty minutes, filtered, and obtained a perfectly limpid solution which contained not a trace of iron.

This experiment proved to my own satisfaction that an accidental excess of 0.25 per cent of iron in fresh black could not be charged with creating irregularities in the process of refining sugar liquors. But not being an expert in sugar refining I submitted this problem with the above results of my own researches to my friend, Dr. Arno Behr, now Secretary and Treasurer of the Chicago Sugar Refining Company, an acknowledged expert in this branch of chemical industry at home and abroad. I submit herewith an abstract of his letter:—

Chicago, Jan. 4, 1892.

MY DEAR DR. TERNE,— . . . "Iron is a very objectionable substance to have in filtered sugar solutions, because the refined soft sugars which are produced from such solutions take on a more or less gray appearance, which reduces their value considerably compared with others which are free from iron and of a bright yellow color.

"Colonial raw sugars contain sometimes a considerable amount of iron, and in the absence of good chemical methods for the removal of this iron from the unfiltered liquor, the refiner relies on the bone-black to absorb it.

"In some refineries the sugar solutions enter the black practically neutral, in others they are left a little acid, but this is of no consequence, for you have found yourself that new black will absorb the iron even from a strongly acid solution. Even old working bone-black contains enough carbonate of lime (three to four per cent) to neutralise any considerable excess of acid. There is, however, a considerable difference in the behaviour of new and old black. Say you want to filter 100 pounds of dry sugar over 100 pounds of bone-black. Say this sugar contains two or three-hundredths of one per cent of Fe_2O_3 . The solution will come from the new black absolutely free from iron, while from the old black half of it perhaps will be free, and the other half will contain it in increasing quantities.

"This will happen with properly neutralised liquor and without any fermentation having occurred. Even if the sugar solution enters the black free from iron, towards the end it will come from the old black containing iron.

"It works this way without any attempt having been made to wash the liquor out of the black. As soon as that is done matters become worse. Even from very good black the diluted sugar solution carries away a certain amount of iron.

"Now, in working it is found that the amount of iron increases in the black with its age, and that in the same proportion the amount of iron increases in the liquor. There is no way of removing the iron once absorbed by the black.

"There are three sources of iron in the black:—

- (1). "The iron originally contained in the black.
- (2). The iron in the raw sugar.
- (3). "The iron taken up by the liquors and the bone-black in the sugar refining.

"The liquor has very little chance to dissolve iron, but the bone-black gets more or less of it by its passages through the kilns. The iron in the raw sugar the refiner has to take and make the best of, but in the case of the iron in the new black he will naturally fall back on the bone-black manufacturer and I do not blame him.

"It is reasonable to expect that a black with 0.1 per cent Fe will furnish iron-free liquors for a longer time than one with 0.3 per cent Fe. Most of the iron in new

* From the *Journal of the Franklin Institute*, April, 1892.

bone-black is in the metallic state and can be removed by running the crushed black over a magnetic separator.

"With best regards,
"Yours very truly,
"ARNO BEHR."

Certainly every one will agree with my friend Dr. Behr that 0.1 per cent impurity of anything is to be preferred to 0.3 per cent; the self-interest of the manufacturer will command the adoption of such means as to keep the percentage of iron as low as possible.

In the interest of manufacturers of bone-black everywhere, I thought it, however, of sufficient importance to refute the theory that an accidental excess of a fraction of a per cent over the acknowledged unavoidable proportion of iron in new black could be held accountable for any disturbance in the process of sugar refining, and to have my protest recorded with the section against such a claim.

This point has been fairly covered by my own experiments, and is clearly corroborated by the opinion of one of the most competent sugar chemists of this country.

Regarding the chemical methods of iron determination which are far too laborious to perform every day, I have been trying to find a method which could be carried on with sufficient accuracy without requiring previous chemical training.

I found that a boy, with the help of a magnet, could, by exercising the necessary care, make a determination sufficiently accurate for the daily control of a bone-black mill.

Take 100 grms. of the black and spread it in a thin layer over a sheet of white paper, then plough through it with a good magnet (I am using a six-inch horseshoe) and it will be found that most of the iron will be picked up at the first few passes.

After repeating the passes of the magnet in every direction, carefully observing that no part of the mass is missed, in a very few minutes all the iron will have been gathered upon the watch-glass ready for weighing. The results thus obtained come sufficiently close to those obtained by chemical test to serve as a control upon the process of manufacture, as the following examples will show.

The following tests have all been made within the last four months:—

	By Chemical Analysis. Per cent Iron.	By Magnetic Test. Per cent Iron.
October, 1891	0.360	0.410
" 1891	0.160	0.219
December, 1891	0.387	0.501
January, 1892	0.100	0.130
" 1892	0.169	0.213
" 1892	0.080	0.107
" 1892	0.199	0.224

While the magnetic test is invariably too high, it is sufficiently close to control the work of the black mills. The adherence of particles of carbon to the iron fully explains this result.

Regarding the chemical determination of iron, I consider a previous incineration of the black necessary, because there is a possibility that traces of organic matter left in the fresh black may be mistaken for iron by the reduction of the potassium permanganate.

Study of the Ammonium Chromates in order to obtain Ammonium Protioxide (or Trihydrazine, &c.), H_3NO .—E. Maumené.—The author refers to and continues certain researches of Vauquelin, Mohr, and Richter, concerning the neutral ammonium chromate. He hopes to continue these studies, and obtain a simple method of obtaining H_2N .—*Bulletin de la Soc. Chimique de Paris*, No. 6, 1892.

THE CHEMICAL ANALYSIS OF ALUMINUM.*

By ALFRED E. HUNT, G. H. CLAPP, and J. O. HANDY.

THE principal impurities found by us in commercial aluminum have been silicon, iron, and copper.

The present system of valuation of aluminum is based, chiefly, on the *total percentage of impurities*, but account is also taken of their *nature and relative amounts*.

Solubility of Aluminum.

Hydrochloric acid (sp. gr. 1.2) dissolves aluminum, in the form of drillings or chips, with very great rapidity. Sudden foaming up takes place, and much heat is produced. As this foaming often causes overflow, it is desirable to use a more dilute acid for analytical work. A mixture of 35 per cent hydrochloric acid (sp. gr. 1.2) and 65 per cent of water is better suited for general work.

Nitric acid (sp. gr. 1.42) when cold appears to have no action on aluminum. In boiling acid, however, the metal is very slowly dissolved.

Nitric acid (sp. gr. 1.2), similarly, has little or no action when cold. At the boiling point it dissolves aluminum slowly.

Sulphuric acid (sp. gr. 1.84), acting on aluminum, in the cold, soon forms on its surface a coating of sulphate, which protects the remaining metal. When heated, concentrated sulphuric acid dissolves aluminum slowly.

Dilute sulphuric acid, containing 25 to 50 per cent of concentrated acid, dissolves aluminum, in the cold, but only after a long time. Heating hastens the solution to such an extent that we have hopes of using this method of attack in determining iron hereafter.

Aqua regia, even that which contains only one-sixth as much hydrochloric acid as nitric acid, and a volume of water equal to that of the mixed acids, dissolves aluminum *almost completely* without warming and *fully* when heat is applied.

Potassium hydrate solutions of various strengths dissolve aluminum readily.

F. Regelsberger (*Zeit. fur angewandte Chemie*, June, 1891) uses potassium hydrate, usually in 40 per cent solution, as a solvent in the processes by which he analyses aluminum. 1 grm. of aluminum requires for solution about 15 c.c. of the 40 per cent KOH.

We do not favour this solvent for general work. Its use prolongs the analysis and renders close attention a necessity. The fatal objection, however, to its use in a laboratory where large numbers of aluminum analyses are to be made is its expense. It would cost three times as much as the acid processes which we employ,

Silicon.

a. *Properties of Silicon in Aluminum*.—In planning a method for determination of silicon in aluminum it is necessary to remember that it exists therein in two forms, the graphitoidal or crystalline and the combined form.

Properties of Graphitoidal Silicon.

When commercial aluminum is dissolved in any acid or mixture of acids, graphitoidal silicon remains behind, mixed with more or less silica. Our experiments show that this graphitoidal silicon has the following properties:—

a. It is oxidisable only to a slight extent by heating over a Bunsen burner or blast lamp. Oxidation proceeds slowly, even if the mass is frequently stirred.

We found that 0.1114 grm. of a mixture of silicon with a very small amount of silica gained 0.0050 grm. in one hour over a Bunsen flame.

In a second experiment, 0.0908 grm. of a mixture of silicon and silica (half and half) gained 0.0018 grm. in fifteen minutes, heating over a blast lamp.

* *Journal of Analytical and Applied Chemistry*, vi., No. 1.

TABLE I.
Separation of Silica from Silicon by Sulphuric and HF Treatment.

	No. 491. Grm.	No. 483. Grm.	No. 499. Grm.	No. 602. Grm.	No. 475. Grm.	No. 475. Grm.	No. 475. Grm.
Original weight silicon and silica	0'0218	0'0341	0'0183	0'0132	0'0909	0'0908	0'0297
Loss of weight by first HF treatment	0'0029	0'0136	0'0051	0'0041	0'0453	0'0460	0'0147
" of first residue by HF treatment..	0'0039	0'0067	0'0020	0'0004	0'0094	0'0167	0'0061
" of second residue by HF treatment		0'0057	0'0021	0'0009	0'0097	0'0098	

Oxidation by heating alone is therefore too slow to be of use analytically.

b. Graphitoidal silicon is gradually oxidised and dissolved by heating with 40 per cent potassium hydrate solution.

c. Fusion with sodium or potassium carbonate or nitrate quickly oxidises graphitoidal silicon and produces the corresponding silicate.

d. Notwithstanding the difficulty of oxidising graphitoidal silicon *completely* by heating it in the air, its *partial* oxidation by this means is sufficient to interfere seriously with any method which depends for success on its permanency, even for a short time.

Thus, when at the end of the first step in the determination of total silicon we obtain a mixture of silicon and silica, it would seem to be a very simple procedure to treat this weighed mixture with a few drops of sulphuric acid and 3 to 5 c.c. of hydrofluoric acid, evaporate, ignite, and weigh the *residual silicon*.

Unfortunately, as the experiments show, the determinations are not so simple. Of course, all the silica which was originally present has been volatilised by the hydrofluoric treatment, but we have left a *residue of silicon and silica* from the oxidation of a part of the original graphitoidal silicon. Having thus discovered that part of the graphitoidal silicon has been oxidised, we are left in doubt whether some silica from that source also has not been volatilised by the hydrofluoric acid treatment. Our experiments show that it has.

Thus, the apparent loss of weight by the HF treatment is made up of silica (originally present), plus silica from oxidation of graphitoidal silicon, and minus oxygen taken up by graphitoidal silicon. Table I. gives the results of experiments by this method, *first* on the original mixture of silicon and silica, and *then* on the residues from the $\text{H}_2\text{SO}_4 + \text{HF}$ treatment of the mixtures.

Thinking that better results might be obtained by washing the silicon out of the mixture by the use of dilute hydrofluoric acid alone, a few experiments were made. The weighed mixture of silicon and silica in a platinum crucible was stirred with 5 c.c. of Baker and Adamson's C.P. hydrofluoric acid, till lumps were disintegrated. Two parts of water were then added, and the mixture filtered. One wash was given with a mixture of 30 per cent hydrofluoric acid and 70 per cent water, and then a number of washings with water sufficient to remove the acid. The filter paper was then burned off and the residue weighed. Repetition of the washing, &c., showed that the graphitoidal silicon had been oxidised to a slight extent during the short heating required to burn off the filter paper.

TABLE II.
Separation of Silica from Silicon by HF Wash.

	No. 419. Grm.	No. 427. Grm.	No. 443. Grm.
Original weight of silica and silicon	0'0454	0'0561	0'0492
Loss of weight by first HF wash	0'0094	0'0123	0'0120
Loss of weight of residue from first treatment by second HF wash	0'0027	0'0018	0'0011

It is probable that the oxidation of the residual graphitoidal silicon can be wholly avoided by drying it on a weighed filter instead of attempting to burn off the filter paper, but we found that this would be impracticable for

general work, because of the difficulty of weighing a number of filters under exactly the same conditions before and after HF washing.

We are now preparing to test for a method of filtration of the silica and graphitoidal silicon upon a platinum filter made in the form of a truncated cone, which will fit closely in the base of a platinum Gooch filter, or in such a filter without the perforated base. The scheme being to weigh the filter after washing the silica and silicon mixture with hot dilute hydrochloric acid and water, and finally with hot water and drying at 80° C., treating with hydrofluoric acid and sulphuric acid to dissolve the silica. Wash with hot water and weigh again without delay after drying at 80° C., the loss in weight being the silica in the mixture, and the residue being the graphitoidal silicon. This method bids fair to prove approximately accurate. The platinum truncated cone is being made as an enclosed box of platinum sheet soldered around a mass of an alloy of platinum and zinc, the top and bottom surfaces being perforated with fine holes for the passage of the liquids through it, the zinc being dissolved out of the alloy with sulphuric acid, leaving the interior of the cone a mass of platinum sponge to act as a filter. The filter can be cleaned from the graphitoidal silicon by immersing it in a mass of molten sodium carbonate in a platinum crucible, which will transform the silicon into silica, in which condition it can be washed out with hydrofluoric acid.

Combined Silicon.

A portion of the silicon in aluminum exists in the combined form.

The ratio of combined to graphitoidal silicon is, according to our experience, less the more silicon the metal contains.

Determination of Total Silicon.

0'9334 gm. of thin turnings or drillings are placed in a 4-inch evaporating dish. 15 c.c. of nitric acid (specific gravity 1'2), and 2 c.c. of concentrated hydrochloric acid are added and mixed, and the dish covered with a glass.

Solution takes place when evolution of NO_2 (hyponitric) fumes, showing that the conditions favour oxidation of combined silicon. In a few minutes, when action has nearly ceased, about 2 c.c. more of concentrated hydrochloric acid are added. This completes the decomposition of all except the very pure grades of aluminum. These require warming with the acid mixture for a time.

After the aluminum has dissolved, 20 c.c. of concentrated sulphuric acid are stirred in and the mixture evaporated quickly, on a hot plate, till it gives off fumes of sulphuric anhydride. The dish is removed before the aluminum sulphate separates and spirits.

After allowing it to cool for a few minutes, 75 c.c. of water and 10 c.c. of hydrochloric acid are added to the contents of the dish, and the whole well stirred. After boiling up for about five minutes, filter off the mixture of silicon and silica and wash with water, next with hot hydrochloric (30 per cent) acid, and finally with water till free from acid.

The filter paper is then burned off and the residue fused with about 3 grms. of sodium carbonate or fusion mixture. Cool the crucible containing the fusion by placing it in 25 c.c. of water in a 4-inch evaporating dish. Cover the dish, and add sufficient concentrated hydrochloric acid to decompose the fusion; when effervescence ceases, rub, and wash silica off from surfaces of crucible and cover, and remove the latter from the dish.

Add 15 c.c. concentrated sulphuric acid, and boil down the mixture to sulphuric fumes, on the hot plate.

After cooling sufficiently, add 75 c.c. of water and 10 c.c. of concentrated hydrochloric acid, boil up and filter. Wash thoroughly with water, 30 per cent hydrochloric acid, and finally water. Burn off, and weigh silica. As 0.9334 grm. of aluminum were taken for analysis, the weight of silica in grms. less the silica obtained from the fusion mixture divided by 0.02 equals per cent of silicon (total). We have many times treated with HF silica thus obtained and have always found it pure.

Our reasons for using sulphuric acid to dehydrate the silica are its rapid action compared with evaporation to dryness, and its leaving the silica in a form which filters easily. Evaporation of hydrochloric and nitric acid solutions to dryness fails to fulfil these requirements.

Determination of Iron and Copper.

1 grm. of aluminum is dissolved in 40 c.c. of a mixture of 33 per cent concentrated hydrochloric acid with 67 per cent water. When solution has been effected, boil up, dilute with warm water to 250 c.c., and pass sulphuretted hydrogen into the solution till saturated.

Filter off silicon, sulphide of copper, &c. The copper is separated from the residue and determined by any of the well-known methods. For instance, having obtained the copper in nitric acid solution from the ignited residue in which the silica has been rendered insoluble, the latter solution can be evaporated to dryness, and after ignition the residue of cupric oxide weighed. The copper may also be determined by battery precipitation from a dilute sulphuric acid solution.

The iron in the filtrate, from the precipitation with H_2S , is estimated by titration (after boiling down the solution to 50 c.c.) by means of standard potassium bichromate. We use stannous chloride to reduce the Fe_2Cl_6 , and mercuric chloride to take up the small excess of stannous chloride.

The metallic aluminum is usually obtained by difference in our commercial work, as we find that commercial metal made by electrolysis of alumina dissolved in molten fluoride salts very rarely contains any solid impurities other than silicon, iron, and copper. In some cases we have found sodium or potassium present, which we have separated and determined as in well-known methods of analysis for the alkalis in fire clays.

Determination of Aluminum.

The determination of aluminum in the commercial metal by difference is only approximate, for not only may there be alkali metals, but considerable amounts of occluded gases present to cause erroneous results, as well as the errors in determining the amounts of silicon, copper, and iron present.

In all important work we determine the percentage of metallic aluminum gravimetrically by precipitation, with hyposulphite of soda. The details of the method are as follows:—

1 grm. of aluminum is dissolved in about 25 c.c. HCl (35 per cent strong acid), and evaporated to dryness. It is then re-dissolved in dilute HCl by boiling, and is filtered from silica and silicon. The filtrate is diluted, warmed, and saturated with H_2S . CuS is filtered off and washed with H_2S water. The filtrate is boiled till free from H_2S , and made up to 250 c.c.; 50 c.c. of this solution are nearly neutralised with NH_4OH . Then 5 c.c. of saturated ammonium phosphate and 10 c.c. saturated sodium hyposulphite are added and the solution boiled till free from SO_2 .

Filter and wash with hot water. Re-dissolve the $AlPO_4$ in dilute HCl, re-precipitate with slight excess of ammonia and a little phosphate, and boil.

Filter, wash, ignite in porcelain, and weigh as $AlPO_4$ containing 22.36 per cent aluminum.

Titanium and Chromium Alloys.

Titanium and chromium are added to aluminum to give hardness and resilience to the metal. Chromium gives the best results for hardness in castings. Titanium imparts more toughness and resilience, and is added when the metal is to be worked after being cast.

(To be continued.)

OBITUARY.

THE LATE GEORGE HOGARTH MAKINS.

GEORGE HOGARTH MAKINS was born in 1815. He was educated for the medical profession, and passed the usual qualifying examinations, but he never practised. His tastes were from the first strongly directed towards chemistry, which he had the advantage of studying under Prof. Daniell, of King's College. After qualifying as a medical practitioner, he was successively lecturer on chemistry at the Aldersgate School of Medicine, and at the School of Middlesex Hospital. For a few years, 1849—1852, he carried on the manufacture of pure chemicals at Surbiton, and during this time prepared, by a process of his own, a considerable amount of spongy gold for the use of dentists. At the recommendation of Mr. Field, Assayer to the Mint, he then came to London, and after a preliminary study in the laboratory at the Mint, opened an assay laboratory in Coleman Street. This work proved a great success. He was soon appointed Assayer to the Bank of England, and afterwards made their referee. Mr. Makins introduced a number of improvements into the process of assaying. He designed a new balance which was described at the Chemical Society in 1852; he gave up the use of "trial plates," substituting for them pure gold and silver; he improved the apparatus employed for "acid parting"; he abolished the charcoal furnace, and substituted anthracite as the fuel. In 1863, Mr. Makins was obliged by ill-health to retire from the assay laboratory; he continued to give a short annual course on metallurgy at the Dental Hospital in Leicester Square till 1880. These lectures were enlarged and republished as a "Manual of Metallurgy" in 1862; a second edition, much increased in size, was brought out in 1873. Mr. Makins was elected a Fellow of the Chemical Society in 1845, and served repeatedly on the Council. He was an original Fellow of the Institute of Chemistry, and was a member of the Council at the time of his death.

Chemistry by no means absorbed the whole of Mr. Makins' energy; he was an amateur architect of considerable experience, and a thorough musician. He was devoted to the organ, and constructed himself three organs in the course of his life. Later in his life a new sphere of activity was opened to him. He was elected in 1880 to the Court of Assistants of the Society of Apothecaries, and for twelve years was most assiduous in his endeavours to promote the welfare of the Society. He became Master in 1889.

Mr. Makins retained his activity till a few months before his death, which took place on April 12, 1892. Mr. Makins was much esteemed by those who knew him. He was methodical and painstaking in his work, and of a very kindly disposition.

"Chemistry a French Science."—"History of Chemistry,"—so-called,—compiled by M. Jagnaux, and ably, though severely, reviewed in the *Chemiker Zeitung*, is avowedly written to demonstrate the dictum quoted above.

Action of Metals upon Salts dissolved in Organic Liquids.—Raoul Varet.—Certain metals capable of precipitating others from their salts dissolved in water lose this property if we substitute for water certain organic liquids.—*Bull. de la Soc. Chim. de Paris*, No. 6, 1892.

CORRESPONDENCE.

ON THE PREVENTION OF BUMPING.

WHEN the presence of a heavy precipitate occasions bumping it is only requisite to keep it in suspension by mechanical means or by rapid ebullition to stop the bumping. Excluding cases of this kind bumping may take place in *homogeneous* liquids of alkaline, acid, or neutral reaction, and is due to the practical absence of air or gas from the liquid. Again, bumping takes place when *non-homogeneous* or immiscible liquids are attempted to be boiled or distilled together. However diverse these classes may appear, the ultimate cause of the bumping, I believe, is identical; so that preventive means ought to be equally efficacious in homogeneous or non-homogeneous liquids.

The only rational method for preventing bumping is to aerate the liquid; but the usual method of effecting this by bubbling air or gas through the bumping liquid is only of occasional benefit, and often worse than useless. Aëration, with its consequent prevention of bumping, is best accomplished by the slow and minute evolution of some insoluble gas in the liquid under operation. This can be elegantly accomplished in all cases where the liquid is an electrolyte by passing a current of electricity through it. The battery wires, which terminate in thin platinum wires, may be introduced inside a piece of glass tube, the end being fused, so that only the platinum wires (1 inch long) are in contact with the liquid.

The same slow and efficient aëration may be also accomplished by the introduction of some substance, best in fine powder, which will interact with the liquid and slowly evolve gas. For this purpose many metals may be employed, *e.g.*, zinc dust is widely applicable, evolving hydrogen in acid, alkaline, aqueous, and alcoholic solutions.

The addition of a minute quantity of zinc dust when estimating NH_3 by expulsion with NaHO , completely prevents all bumping. As in this case regard must be taken of the action of zinc on nitrate and nitrate-free NaHO used, so in all cases the secondary reactions must be carefully considered.

Methylated spirit, which can scarcely be used now without purification, distils quietly from all sorts of mixtures (as when recovering) on the addition of a little zinc dust.

Again, when it is attempted to distil mixtures of oil and water, or tar and liquor, recourse is generally had to heating and separating to get rid of as much liquor as possible before a troublesome distillation begins. However, by the simple addition of a grain or two of moistened zinc dust, mixtures of oil and water or liquor, in all proportions, may be distilled quietly in a flask of little more than double the capacity of the mixture taken. If necessary, the addition of zinc may be repeated, and if the solution is purely aqueous, a minute quantity of alkali may be added with benefit if permissible.

These examples will suffice to show how the principle may be employed in any case.—I am, &c.,

GEORGE CRAIG.

Lugar Iron Works, Cumnock, N.B.

DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILISERS.

To the Editor of the Chemical News.

SIR,—In reading the articles on "The Determination of Available Phosphoric Acid in Fertilisers containing Cotton-Seed Meal" (CHEMICAL NEWS, vol. lxx., pp. 163 and 170), I note that no mention is made of the probable formation of pyro-phosphates in the author's "incineration method." It is, I believe, generally acknowledged

that the ash of organic manures is *not* available for the determination of phosphoric acid on this very account. I quote a few lines:—"It is believed that the disparity in all these cases is probably not so great as it should be; that is to say, that the incineration method as here used probably does not give the full content of phosphoric acid for this reason. The inferiority of the solvent power of nitric acid for phosphates to that of hydrochloric acid is well recognised. I believe that this inferiority is greater when the phosphate has been ignited."

I offer the formation of pyro-phosphates as a further and probably more serious source of error in the incineration method.

We have it on the authority of Fresenius that even fusion with alkaline carbonates fails to completely convert pyro-phosphates of the alkaline earths into ortho-phosphates with the exception of magnesian pyro-phosphate. I should myself incline to the direct solution in hydrochloric acid and potassium chlorate, but have no practical experience of cotton-seed meal fertilisers.—I am, &c.,

WALLIS JENKINS, F.C.S.

5, Bishop Lane, Hull, May 3, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

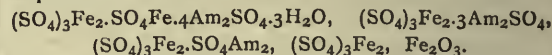
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 15, April 11, 1892.

Researches on Persulphuric Acid and its Salts.—M. Berthelot.—Much of this paper is a reproduction of a memoir read by Mr. H. Marshall before the Chemical Society, and to be found in its *Transactions* for 1891.

The Decomposition of Silver Permanganate and a Peculiar Association of Oxygen with Silver Oxide.—Alex. Gorgeu.—The author's conclusion is that there exists between metallic oxides and oxygen a kind of association distinct from that known as occlusion, and in the state of combination properly so-called. The distinctive character of this association is to produce when broken up by the action of acids the separation of the whole or of a part of the oxygen over and above that of the protoxide in a form as inactive as that of the gas when in a free state.

On New Salts of Iron.—MM. Lachaud and C. Lepierre.—The bodies obtained are—



These compounds have been obtained by melting a mol. of ammonium sulphate and a mol. H_2SO_4 to tranquil fusion (melting-point 121°), projecting into the liquid about one-fifth part of ferrous sulphate or of ammonium ferrous sulphate or even of iron-filings; the mixture is heated gently to expel the chief part of the water, and the application of heat is continued for a longer or shorter time according to the cases. Under these conditions several crystalline salts are formed in succession, for the most part insoluble in cold water, which, however, attacks them by degrees.

Researches on Certain Saccharine Principles.—J. Fogh.—A thermo-chemical paper, which does not admit of useful abstraction.

Action of Sulphuric Acid upon Certain Cyclic Hydrocarbides.—M. Maquenne.—Contrary to its usual manner of acting, sulphuric acid is capable of bringing certain cyclic carbides of the terpene family to the state of maximum hydrogenation. This hydrogenisation appears to be correlative with the escape of sulphurous

acid which always accompanies it. This is a further analogy between heptene and the true terpenes.

The Formation of Oxyhæmoglobine by means of Hæmatine and an Albumenoid Substance.—H. Bertin-Sans and J. Moitessier.—Under the conditions specified by the authors, hæmatine unites with the albumenoid matter of oxyhæmoglobine, forming at first methæmoglobine and then oxyhæmoglobine, unless, which does not appear probable, a mixture of hæmatine and of albumenoid matter could give the appearances and the complete series of spectral reactions which characterise hæmoglobine and its immediate derivatives.

Vol. cxiv., No. 16, April 19, 1892.

This issue does not contain any chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 6.

On the Solubility of Tricalcic Phosphate and Bicalcic Phosphate in Solutions of Phosphoric Acid.—H. Causse.—It appears from the author's researches that tricalcic phosphate dissolves in solutions of phosphoric acid in a much larger quantity than bicalcic phosphate. The cause of this difference seems to reside in an equilibrium which is established between three factors, water, phosphoric acid, and monocalcic phosphate. The water seems to play the principal part; it distributes its action between the monoclinic phosphate and the phosphoric acid, and everything depends on the proportion of these two compounds. The maximum quantity of dissolved phosphate corresponds to a solution containing 10 per cent of dissolved acid.

Cyanogen Compounds of Magnesium.—Raoul Varet.—The action of magnesium iodide upon mercury cyanide yields a compound of magnesium cyanide with mercury iodocyanide. The action of magnesium bromide upon mercury cyanide produces a compound of the same order.

On Metaphenyltoluene.—G. Perrier.—Already inserted.

Relation which Seems to Exist between Acid or Saline Solution, and the Molecular Weights of the Dissolved Substances.—Antoine de Saporta.—This paper does not admit of useful abridgment.

The Action of Carbon upon Alkaline Sulphates in Presence of Silica and of Carbon upon Sulphurous Acid. Application to the Production of Soluble Silica and of Glass.—Scheurer-Kestner.—The decomposition of the alkaline sulphates by silica and charcoal may be formulated according to the general equation:—

$(\text{SO}_4\text{R}) + 6(\text{SiO}_2) + 5\text{C} = 3\text{S} + 4\text{CO}_2 + \text{CO} + 3(\text{RO}, 2\text{SiO}_2)$,
the gases escaping consisting exclusively of free sulphur, carbon dioxide, and carbon monoxide.

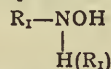
Concentration of Sulphuric Acid in Apparatus composed of Cast-Iron and Platinum.—Scheurer-Kestner.—The author proposes the combination of two systems. The one consists in the use of a boiler of cast iron with a dome of platinum; the second in the employ of Kessler's well-known tanks, the first of platinum and the second of cast-iron. He has combined the two systems in one, composing an apparatus formed of platinum tanks, of Kessler's kind, preceding an apparatus with a cast-iron bottom. The greatest difficulty has been in joining the metals together. It has been overcome by the combined use of platinum, cast-iron, and lead connected with asbestos joints. Cast-iron is less attacked by acid at 95 per cent than by either stronger or weaker qualities.

The Colorimetric Determination of Iron.—J. Riban.—A controversial paper in reply to M. Lapique (*Bull. Soc. Chimique*, ii., p. 295).

An Isomer of Chromium Sesquioxide.—A. Recoura.—Already noticed.

Journal für Praktische Chemie.
New Series, Vol. xlv., Nos. 23 and 24.

The Action of Sulphurous Acid upon Isonitroso-Compounds.—M. Schmidt.—If the results obtained by the author's researches are briefly summarised it appears that in the isonitroso-compounds of the composition—



therefore alkyl derivatives of hydroxylamine sulphonyl enter in place of hydroxyl, with the formation of substituted amidosulphonic acids. The compounds of the general formula $\text{R}_1\text{—NOH}$ may be arranged in three classes according to their behaviour with sulphurous acid. 1. Such as are very easily soluble in solution of sodium bisulphite, and form with it amidosulphonic acids so readily soluble that they do not separate from the solution or are readily oxidised, with the formation of brown masses, e.g., nitrosophenol, nitrosoresorcin, &c. 2. Such which dissolve in solution of sodium bisulphite on boiling, and from the solutions of which, if decomposed with hydrochloric acid, amidosulphonic acid are separated. The formation of such compounds is accompanied by a reduction analogous to that which takes place on the conversion of quinone into hydroquinone. Of the three nitroso-naphthols only the two, α and β , substituted are transformed by sulphurous acid in this manner, not the α -nitroso- α -naphthol. 3. Such isonitroso-compounds— $\text{R}_1\text{.NOH}$ —can be distinguished which are not attacked by sodium bisulphite at all, e.g., nitrosothymol, ethylnitrolic acid.

Communications from the Chemical Institute of the University of Kiel.—Th. Curtius and L. Pflug.—These comprise: "Preparation of Secondary Asymmetric Hydrazines by the Action of Aldehyds or Ketones upon Hydrazinhydrate," and "Substitution of Keto-Oxygen by the Azo-Group N_2 ," by Th. Curtius and Hans Lang.

Minor Communications from the Laboratory of E. von Meyer.—These comprise a memoir by P. S. Burns on the "Dimolecular Nitriles," a paper by H. Thiesing on "Methylendibenzamide and Analogous Compounds," and a note by H. Fleischauer on the "Condensation of Cyanides with Esters."

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. viii., No. 75.

Purification of Water.—Prof. A. R. Leeds.—From the CHEMICAL NEWS.

The Greenwood Process for the Direct Production of Chlorine and Caustic Soda.—From the CHEMICAL NEWS.

Fundamental Principles of the Chemical Analysis of Wines.—Prof. Fresenius and Herr Haas.—From the CHEMICAL NEWS.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Respiration of Plants and Animals.—In many books on Elementary Chemistry one finds it stated that animals exhale carbonic acid gas, and that trees and plants, &c., inhale it, retain the carbon and exhale the oxygen. In Sachs' "Botany" it is stated very plainly that plants exhale carbonic acid gas in considerable quantity. Can you kindly recommend any book explaining this apparent contradiction?—I. L.

MEETINGS FOR THE WEEK.

- MONDAY, 9th.—Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Industries," by Percy F. Frankland, F.R.S. (Cantor Lectures).
- TUESDAY, 10th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
— Royal Institution, 3. "Photography in the Colours of Nature," by Frederick E. Ives.
- WEDNESDAY, 11th.—Society of Arts, 8. "Uses and Applications of Aluminium," by G. L. Addenbrooke.
— Geological, 8.
- THURSDAY, 12th.—Royal, 4.30.
— Royal Institution, 3. "The Chemistry of Gases," by Prof. Dewar, F.R.S.
— Institute of Electrical Engineers, 8.
— Mathematical, 8.
- FRIDAY, 13th.—Royal Institution, 9. "The New Star in Auriga," by Dr. William Huggins, F.R.S.
— Astronomical, 8.
— Physical, 5. "An Instrument for Drawing Parabolas," by Richard Inwards, F.R.A.S. "Some Electrical Instruments," by F. H. Nalder. "An Instrument for Measuring Magnetic Fields," by E. Edser and H. Stansfield.
- SATURDAY, 14th.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Dannreuther.

TO CORRESPONDENTS.

H. S. L.—A simple chemical calculation will give you the information you ask for.
R. W. Tubb.—See a paper by Grace-Calvert and Johnson "On the Action of Sea Water on certain Metals in the CHEMICAL NEWS, vol. xi., p. 171.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1694.

REPORT ON PHOSPHORIC ACID.*

By W. B. BURNEY.

ADOPTING the usual method of reporting on phosphoric acid, the subject will be presented in the following order: (1) Condensed abstracts of methods published during the year; (2) results of work done by members of the association and others; (3) recommendations for the next year.

ABSTRACTS.†

The Estimation of Phosphoric Acid by Ammonium Molybdate.‡

For the titration of phosphoric acid by molybdate, the latter should be acidified with three to four molecular proportions of nitric acid to one of molybdic acid, while the phosphate solution is only slightly acidified. Under these conditions one molecular proportion of phosphoric anhydride is exactly precipitated by twenty-four of MoO_3 . Ten grms. of molybdic acid (or 12.262 grms. of crystallised hexammonium heptamolybdate) is dissolved in an excess of dilute ammonia, the solution neutralised, further acidified with 15 grms. nitric acid, and diluted to 1 litre. 24.3 to 24.5 c.c. precipitate 0.01 grm. P_2O_5 .

For gravimetric determinations the author considers Finkener's method the best. The washed precipitate is dissolved in warm dilute ammonia, the solution evaporated until most of the ammonia is expelled, then mixed with an excess of nitric acid, evaporated, and heated to complete decomposition of the ammonium nitrate, the final temperature being about 180° . The residue contains 3.753 per cent P_2O_5 .

If the precipitate has been washed with neutral ammonium nitrate, it may be titrated as follows:—It is stirred up with cold water containing phenolphthalein, and mixed with standard soda until it has completely dissolved and the liquid is red. It is then rapidly titrated back with nitric acid. One c.c. N/10 soda = 0.00061739 grm. P_2O_5 .

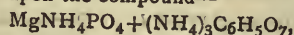
Analysis of Concentrated Superphosphates.§

This superphosphate generally has from 4 to 5 per cent of P_2O_5 as ferric or aluminic phosphate, which is insoluble in water, but soluble in concentrated solutions of superphosphate. It is therefore important to use sufficient water in the first extraction, otherwise the soluble P_2O_5 will be reported too high. Take 1.5 grms. of the superphosphate, place in a beaker, and add a little water to soften and break up the lumps. Then make up to 90 c.c. Allow it to stand five minutes, and filter off the supernatant liquid. To the residue add 90 c.c. of water, stir, allow it to settle, and filter. Treat the residue with 60 c.c. of water, warm gently, bring upon the filter, and wash once with hot water.

Citrate Method, Phosphoric Acid Determination.||

The author supposes that the double phosphates with ammonium form soluble compounds with ammonium citrate, and that only the magnesium ammonium phosphate is easily, but never completely, decomposed. To make this as complete as possible, more magnesium chloride than can combine with the ammonium citrate to

form $\text{MgNH}_4\text{C}_6\text{H}_5\text{O}_7$ should be present so that this excess may act upon the compound—



which may have formed. Some MgNH_4PO_4 , however, always remains in solution and causes a loss. When other bases (CaO , Fe_2O_3 , Al_2O_3 , MnO , FeO) are present, their phosphates are somewhat thrown down, and cause an error. With CaO the error is largest. If the lime has been removed by oxalate or sulphuric acid, a loss of P_2O_5 may always be expected if we do not use at least twice the amount of magnesia mixture usually prescribed. Silica always contaminates the precipitate when present. The author considers the molybdenum method more accurate.

In addition to the above article the author notes the following:—

1. Treatment of the substance with hydrochloric acid is objectionable, as the precipitate may contain considerable silica.

2. Treatment with sulphuric acid reduces this error to about 1 m.grm. of silica.

3. Even when an excess of ammonium citrate is present and only little CaO , the precipitate contains from 1 to 2 m.grm. CaO as pyrophosphate.

4. The presence of manganese exerts a similar influence.

5. The error caused by Fe_2O_3 and Al_2O_3 in a sulphuric acid solution is very slight when little silica is present, even when large amounts of these oxides are present; they delay precipitation, however.

6. Small quantities of $\text{Mg}(\text{OH})_2$ are always present; this error is slightest when the separation is made in a solution containing 2.5 per cent ammonia. In a nearly neutral solution, and in the presence of alkaline salts, the error is greatest.

7. The phosphoric acid is always incompletely precipitated.

8. In making a control analysis by the molybdate method, the method of treating substances rich in silica must be regarded.

The average error according to the author is ± 0.128 per cent, the — result where only small quantities of P_2O_5 are present.

With Thomas slags and raw phosphates the results are always too high.

The Use of Phosphoric Acid of Animal or Mineral Origin in the Cultivation of the Sugar Beet.†

The results showed that no difference exists between the superphosphates of either animal or mineral origin.

Estimation of Phosphoric Acid in Slags.

Formation of Tetrahydrated Ferric Phosphate.‡

In eliminating by means of nitric acid the residual hydrochloric acid from slag, which had been treated with the latter reagent to remove silica, a probable source of error is shown by the author in that a tetrahydrated ferric phosphate, $\text{Fe}_2(\text{PO}_4)_2 + 4\text{H}_2\text{O}$, is precipitated as a yellow granular powder. This differs from the normal ferric phosphate resulting from the precipitation of a ferric salt by disodium phosphate in not suffering dehydration at 110° .

Estimation of Phosphoric Acid in the Presence of Silica.§

The author proves by numerous experiments that phosphoric acid may be estimated in the presence of pretty large quantities of silica (solution of soluble glass acidified with hydrochloric acid was employed) when the precipitate of ammonium phosphomolybdate is washed with pure

* From the Proceedings of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.

† These abstracts were prepared by Mr. W. H. Krug, of the Chemical Division, Department of Agriculture.

‡ Hundeshagen, Fres., *Zeitsch. fur Anal. Chem.*, xxviii., 165—172.

§ Hughes, J., *CHEM. NEWS*, ix., 91.

|| Reitmar, O., *Zeitsch. fur Angew. Chem.*, 1889, 702—9, and 1890, 19—25.

* Reitmar, O., *Zeitsch. fur Angew. Chem.*, xc., 196—210.

† Stoklasa, J., *Böhm. Zeitsch. fur Zuckerindustrie*, xiv., 137—142 *Chem. Centralbl.*, 1890, 1, 771.

‡ Arth, G., *Bull. Soc. Chim.* (3), ii., 324—327; *Journ. Chem. Soc.*, March, 1890, 292.

§ Preis, K., *Listy Chem.*, xiii., 153, 154; *Journ. Chem. Soc.*, July, 1890, 825.

cold water. As the liquid runs through the filter turbid at the end, double filters should be used.

Results of Work Done During the Year.

In answer to a circular letter sent out in the spring, forty-four replies were received, and thirty-seven chemists consented to participate in the work on phosphoric acid. It is to be regretted that many of these have failed to analyse the samples sent them. Early in May three samples were sent to each chemist consenting to do the work, and consisted as follows:—

No. 1. A superphosphate.

No. 2. A complete fertiliser.

No. 3. A complete fertiliser containing cotton-seed meal and other substances difficult to oxidise.

These samples were prepared with the utmost care, and no pains were spared to insure absolute uniformity in the materials submitted for examination. The fertilisers had probably been made many months when they were collected for this work. They were first air-dried in thin layers for several days, and after grinding were passed through a sieve of forty meshes to the linear inch; the samples then stood for several days more, and were again mixed, first, in large jars, then by passing through a coarser sieve, and finally by hand on heavy paper, after which they were rapidly bottled and sealed.

From the specimens herewith submitted you may judge of the thoroughness of this work. It does not appear probable, therefore, that the differences in the analytical results presented in the following tables* can be attributed to any lack of uniformity in the samples, or to any dereliction on the part of your reporter.

These tables reveal discrepancies alike discouraging and inexplicable. It does not appear that we have made any advance since last year. That the methods employed in these determinations are trustworthy when properly executed follows from the fact that in the hands of a few experienced analysts the results are fairly within the limits of the working error. The fault, therefore, must be ascribed to the chemist, and is doubtless due to a lack of thoroughness, to a want of scrupulous attention to minute details in the processes of solution, precipitation, filtration, washing, &c. Thus we see results which seem to be too high through incomplete washing of the precipitate of ammonium magnesium phosphate; total phosphoric acid too low, owing to incomplete oxidation in the process of solution; insoluble phosphoric acid too high or too low, because the ammonium citrate solution was too strong or too weak, acid or alkaline, and so on.

Comment in detail upon the analytical data seems unnecessary. A very few words will suffice. In the first place the averages are given for what they are worth, and it is not claimed nor believed that in all cases they correctly represent the percentage of phosphoric acid present in the sample. The results on moisture are noteworthy, and seem to point to some grave oversight in the execution of the official method, if indeed the method was employed in all cases. It would be interesting to know how many of the chemists actually tested the steam closet to see that the temperature approximated 100° C.

With the possible exception of the soluble, the results on phosphoric acid cannot as yet be regarded as satisfactory. So long as experienced analysts differ, in extreme cases, by 0.7 to 0.8 per cent, and from the average or probable truth by 0.3 to 0.4 per cent, it must be admitted that there is room for improvement. Now if we omit from each table three or four of the analyses which seem to be extreme, there still remain a number which differ by the amounts above mentioned. Nor is this discrepancy confined to any one kind of phosphoric acid, but it is in varying degree true of all.

In the opinion of the reporter, the remedy for all this is to be sought not so much in the improvement of the

methods of analysis, as in the increased care with which the details of the methods are executed after having been once adopted by this association.

Believing that changes in the official methods should be made with the greatest caution, and only for the best of reasons, the following recommendations are suggested after much hesitation:—

1. That in the preparation of the solution of water-soluble P_2O_5 the washing be continued until the filtrate measures 300 c.c.

2. That in *Chemical Bulletin*, No. 24, p. 225, the second line from top of page be changed to read as follows:—Filter the warm solution quickly through a $1\frac{1}{2}$ centimetre plaited filter, wash twice with half-strength ammonium citrate solution, and then with water of ordinary temperature.

3. That in all cases of fertilisers containing cotton-seed meal, the solution for total phosphoric acid be prepared by the $Mg(NO_3)_2$ method.

4. That the association advise, in the preparation of the solution of total phosphoric acid, the use of method No. 2 (30 c.c. $HNO_3 + HCl$) for superphosphates and other samples free from organic matter; and the $Mg(NO_3)_2$ method for all cases in which organic matter is present.

It is further recommended that with these changes the present methods of determining phosphoric acid be continued, subject, of course, to modification by the association.

ON THE ISOMORPHISM AND COMPOSITION OF THORIUM AND URANOUS SULPHATES.

I.—CHEMICAL DISCUSSION.

By W. F. HILLEBRAND.

DURING the course of an extended investigation on uraninite (*Bull. U.S. Geol. Survey*, lxxviii., 43, 1889—1890), it was often necessary to decompose the mineral in sealed tubes with sulphuric acid. At first a deposit was generally observed on removing the tubes from the oven, the character of which depended on the concentration of the acid and the presence or absence of thoria in the mineral. In the absence of this earth it took the form of a greenish powder with a strong acid, and of bright green, brilliantly reflecting crystals when a weak acid was used, unless the ratio of liquid to mineral was sufficiently high in the latter case to prevent crystallisation. As might naturally be supposed, these crystals were hydrated uranous sulphate. The best results as regards size of crystals were obtained with an acid containing 1 part of sulphuric acid to 5 or 6 of water by volume. With about 100 parts by weight of such an acid to 1 of the oxide UO_2 , it might pretty confidently be expected that no crystallisation would take place.

In presence of thoria the green crystals still appeared, but they then contained thorium as well as uranium, and accompanying them was a beautiful, white, coherent, spongy mass, extending the length of the tube, and consisting of a network of microscopic needles grouped in radiating bunches. This was likewise a double sulphate of uranium and thorium, resembling in every respect the deposit formed under similar conditions from a solution of thorium sulphate alone, except that when washed, dried, and compacted together, there was a faint greenish tinge to it. Ordinarily the two forms of double salt appeared together, and it even seemed as if under favourable conditions, which have not yet been precisely determined, the crop of green crystals might be increased at the expense of the white deposit. At least, on one occasion, when the heating was prolonged for several days, the latter gradually disappeared, while the former increased in size and number. The white deposit always

* The long Tables which follow are omitted as not being necessary or a comprehension of the processes and the arguments based thereon.—Ed. C. N.]

preceded the green crystals, and by regulation of the proportions of oxide and of acid, and of duration of heating, it is possible in practice to obtain the former alone, if desired.

In order to secure material for exact chemical and crystallographical determinations, recourse was had to the artificially prepared oxides U_3O_8 and ThO_2 , by using which, either alone or mixed in varying proportions, different products were obtained. Neither uraninite nor uranium dioxide, UO_2 , is well adapted for this purpose, because of contamination of the crystals by sulphate of lead in the one case and by undissolved dioxide in the other. Even when using the oxide U_3O_8 , care must be taken to avoid a like result by fine pulverisation and avoidance of excess of oxide as compared with acid. So slightly soluble are the green crystals that over 50 per cent of the dioxide UO_2 in uraninite, or in the oxide U_3O_8 , can generally be obtained as sulphate. Hence it follows that when the dioxide is to be estimated volumetrically, care must be taken to use sufficient dilute acid to render impossible the formation of these crystals. The white, spongy deposit, is not a hindrance to the exact estimation of the dioxide by potassium permanganate, for it dissolves readily in cold water, though with extreme slowness when once it has been compressed.

The green crystals were separated from their mother-liquor in a Gooch crucible, without asbestos felt, with the aid of suction; they were at once washed with hot dilute sulphuric acid, then with alcohol, and finally with ether. They were allowed to dry thoroughly in the air and were analysed in that condition. It was found by experiment that alcohol was practically without solvent action on the sulphates, and that none of the water of crystallisation was removed by it. If both forms of deposition occurred at one time, the spongy one was first removed with great ease by two or three rapid washings with cold water—the network of fine needles being partly dissolved and partly carried through the holes in the crucible by the powerful suction—after which alcohol and ether were used as before. The results of analyses were as follows:

	I.	Molecular ratio.	II.	Molecular ratio.
UO_2	49.18	1.00	48.40	1.00
ThO_2	3.59	—	5.58	—
SO_3	32.08	2.05	31.27	1.96
H_2O	14.18	4.04	14.84	4.13
	99.03		100.09	

A sample of uraninite decomposed by dilute sulphuric acid in a tube at about $170^\circ C$. furnished the product whose analysis is given under I. An earlier and very similar analysis of another preparation may be found on page 50 of the Bulletin cited. The loss is mainly, if not altogether, undetermined lead oxide from included lead sulphate, which accounts in part for the excess of SO_2 found. For No. II. the oxides U_3O_8 , ThO_2 , were taken in such proportion that there should be about six times as much uranium dioxide as of thorium dioxide. Inasmuch as only 0.1622 grm. was available for sulphuric acid and water determinations in this analysis the ratio is not bad. One or two attempts to obtain a product with more thorium and less uranium by starting with correspondingly different proportions of the oxides ThO_2 and U_3O_8 , were unsuccessful, perhaps because of the tendency of thorium sulphate to separate at once in the spongy state, and thus to reduce the amount available for slow crystallisation with the uranium. The specific gravity of No. II. was kindly determined by Mr. L. G. Eakins in alcohol of 0.7956 density. It was found to be 4.563 at $24.3^\circ C$., which, calculated for water at the same temperature as standard, becomes 3.63. The material examined contained 1.04 per cent of the oxide U_3O_8 undissolved, which does not appear in the analysis, and, allowing for this, a density of 7.3 (Clarke's tables), that

of the double sulphate having the given composition is found to be 3.61 at $24.3^\circ C$.

The uranium sulphate, of which the analysis is here given, was obtained by decomposing the oxide U_3O_8 with dilute sulphuric acid in the manner already mentioned. Its density was not ascertained.

	II.	Molecular ratio.
UO_2	53.99	1.00
SO_3	31.94	2.00
H_2O	14.13	3.94
	100.06	

It appears, as was to be expected, that thorium is capable of replacing uranium in the sulphate of the latter which holds in combination four molecules of water. That this is a true case of isomorphism is most fully shown by Mr. W. H. Melville in the crystallographical part of this paper, although the habit of the uranium sulphate differs from that of the double salt.

While, as above stated, failure resulted from attempts to lower the ratio between thorium dioxide and uranium dioxide in the green double salt, it was found that the spongy mass, which almost always formed in the tubes when thoriferous uraninite was decomposed with dilute sulphuric acid, contained a very much higher proportion of thorium, and that by taking the dioxides in varying proportions, double salts of correspondingly different composition could readily be obtained, as is shown by the following analyses:—

	I.	Molecular ratio.	II.	Molecular ratio.
UO_2	34.34	1.00	16.92	1.00
ThO_2	19.84		36.07	
SO_3	31.48	1.95	32.66	2.05
H_2O (diff.) ..	14.34	3.95	14.35	4.01
	100.00		100.00	

Both salts were obtained from a mixture of the oxides U_3O_8 and ThO_2 . In the case of No. II. the proportion was such that the uranium dioxide of the compound U_3O_8 was to the oxide ThO_2 as 2 to 1. It happened that the tube containing this preparation lay unopened for several weeks after removal from the oven, but during this time there had been no perceptible resolution of the precipitate, which on agitation made a thick emulsion with the acid. Both products were thrown on a Gooch crucible without asbestos felt, quickly washed twice or thrice with hot dilute sulphuric acid, and then with alcohol and ether, whereupon they were allowed to dry thoroughly in the air.

There is no reason to doubt the isomorphism of this salt with that formed under similar conditions from thorium alone, but whether these are crystallographically referable to the green crystals before described, or form a new case of dimorphism, must remain undetermined until the crystallographic features of the former are known. In polarised light, the needles of the double salt extinguish apparently parallel to their length.

Such contradictory statements appear in the literature of the subject regarding the composition of thorium sulphate separated from hot acid solutions—some authorities claiming $4\frac{1}{2}$ mols. of water of crystallisation and others only 4—that it is very satisfactory to have evidence like that furnished by the above analyses to throw light upon the question. The tendency of late years has been to admit a mutual replaceability of thorium dioxide and uranium dioxide in chemical compounds, though no direct proof seems to have been heretofore established, and it was therefore reasonable to suppose that the composition of the thorium sulphate in question should correspond with that of the well-known uranous sulphate with 4 mols. of water. In the light of the above analyses there is no room to doubt the complete isomorphism of the two sulphates, and that Demarcay (*Comptes Rendus*, xcvi.

1860) and Roozeboom (*Zeit. Phys. Chemie*, v., 195) were right in accepting the formula $\text{ThO}_4(\text{SO}_2)_{2.4}\text{H}_2\text{O}$, derivable from the more or less incomplete analyses of Berzelius, Berlin, and Chydenius, in preference to $\text{ThO}_4(\text{SO}_2)_{2.4}\frac{1}{2}\text{H}_2\text{O}$, afforded by the more numerous ones of Delafontaine.*

In possible explanation of Delafontaine's high results for water, Roozeboom† very justly remarks that because of its physical character the salt retains much mother-liquor, and that if this be not removed at a temperature above 45°C ., the $9\text{H}_2\text{O}$ salt is formed from it on cooling, so that it is almost impossible not to find too much water. Notwithstanding numerous attempts to prepare the salt $\text{ThO}_4(\text{SO}_2)_{2.4}\text{H}_2\text{O}$ from hot acid solutions as well as from warm neutral ones, I have never myself succeeded in reducing the water to 4 mols., even though the mass of needles was rapidly washed with hot dilute sulphuric acid and then with alcohol and ether, after freeing from mother-liquor by powerful suction on a Gooch crucible without asbestos felt, but my faith in the correctness of the formula with $4\text{H}_2\text{O}$ is not hereby shaken. A further possible cause of high results will appear from the following:—The air-dried salt is said by Delafontaine to be thoroughly non-hygroscopic, and for a given temperature and hygrometric condition of the atmosphere it is true that no change in weight does occur; but if the salt be weighed from day to day, or even twice a day, a very marked gain or loss of weight is observed, depending in degree on the amount of change in the atmospheric conditions. In August and September, when hygrometric and thermometric readings were often high, and marked and rapid changes were not infrequent, this gain or loss sometimes amounted within 24 hours to over 0.5 per cent of the total weight of the salt, and the extreme change during those months reached 1.22 per cent. It is therefore patent that the formula afforded by analysis may materially depend on whether the salt analysed was weighed when the weather was hot and moist or cold and dry.

It may not be out of place here to call attention to a possible cause of the frequent discrepancies noticed in the statements of different writers in regard to the amounts of water given off by different substances when placed over sulphuric acid in a desiccator. No one would deny that sulphuric acid of maximum concentration is superior as a drying agent to the same acid somewhat, if only slightly, diluted; but it is probably not known to every one how much may depend on the strength of the acid used. A case in point is the following:—A thorium sulphate containing, air-dried, 15.22 per cent H_2O , or 4.23 molecules, lost weight over concentrated sulphuric acid in a tightly-closed desiccator, as shown in column I. and as in column II. over acid, which had been in use in another desiccator for a considerable length of time, and was subsequently found to have a density of 1.66. The cases are not rigidly comparable, perhaps because of the different times devoted to the experiments, which were not carried on simultaneously, but they serve to illustrate the point.

This may be considered an extreme case, but it shows plainly the importance of using fresh acid of full strength whenever experiments of this kind are to be made, in order that results may be properly comparable.

Similarly it is improbable that a highly hydrated substance, which loses much of its water at 100°C ., would

I.		II.	
Time in days.	Acid of 1.84 sp. gr. Per cent.	Time in days.	Acid of 1.66 sp. gr. Per cent.
1	3.80	1	2.87
3	2.78	1	0.40
5	1.37	3	0.06
9	0.22	—	—
18	8.17	5	3.33

show as great a loss when dried in an ordinary air-bath as in a current of dry air of that temperature.

Another point to be considered when it is desired to find the maximum amount of water that can be removed by any drying agent in a desiccator (which, of course, as a method, is in general inferior to that in which a continuous current of dry air or other gas is passed over the substance) is that, if many days are required for its removal—in other words, if the substance is slow to part with its moisture—the later weighings should not be made from day to day but at ever-increasing intervals, otherwise a prematurely constant weight or even an increase may be observed. This is due to the fact that whenever the desiccator is opened, which must be twice for each weighing, it, at least in the upper part, becomes filled with moist air, and the substance itself may absorb some moisture before it can be returned to the desiccator; one or more days may then be required to restore the condition of equilibrium which obtained between the vapour tensions of water in the salt and in the air of the desiccator prior to opening the latter. Especially if the acid has become somewhat weakened it is possible for an increase to take place.

Originality is not claimed for the above observations on methods of drying, but it seems as if attention could not be too strongly or too frequently drawn to the points mentioned, which there is reason to fear are not always observed.—*American Chemical Journal*, xiv., No. 1.

A COMMERCIAL METHOD FOR THE CONVERSION OF MINERAL ANTIMONITE INTO THE ORANGE COMPOUND.

By H. N. WARREN, Research Analyst.

As is well-known, the mineral sulphide of antimony has been frequently employed in the laboratory as a source for obtaining pure gaseous SH_2 by the action of hydrochloric acid upon that substance. By careful observations it will be found that the mineral substance is somewhat more soluble in hot hydrochloric acid than the orange compound; and by taking advantage of this property, the author has supplied a method for the conversion of that substance into the orange compound, adapting the same as a pigment. In arranging for this reaction hydrochloric acid is so diluted as to allow, when raised to the required temperature, an exact solution of the antimonite employed. The solution so formed should now, upon the addition of SH_2 , precipitate the whole of the antimony as the orange sulphide; the acid thus set free being employed for a further use with a fresh addition of mineral.

The apparatus employed consists of a convenient sized retort, into which is introduced the required quantity of mineral along with its accompanying solvent, and heat is applied so as to maintain a steady evolution of gas.

To the retort is connected several suitable receptacles containing a quantity of already prepared solution of antimony chloride, and the issuing gas from the retort allowed to traverse the whole; the orange compound thus precipitated is filtered from its acid solution, washed and dried, and the filtrate so formed returned to the converter for continued action upon a further quantity of mineral.

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18, Albion Street, Everton, Liverpool.

* *Ann. Chem.* (Liebig), cxxxi., 100. The statement by Kraut, near the foot of page 637 of "Gmelin-Kraut's Inorganic Chemistry," Vol. II., Part 1., is manifestly unwarranted. He considers the evidence in favour of the $4\text{H}_2\text{O}$ salt as insufficient, and thinks the analyses affording this formula were made upon mixtures which might have resulted through absorption of water by the $3\text{H}_2\text{O}$ salt. It is strange that individuality should have been accorded by Chydenius and Cleve to this latter salt, which the former obtained by drying over sulphuric acid, after washing with hot water, the precipitate formed by boiling a weakly acid solution of the sulphate. Roozeboom is certainly correct in excluding this $3\text{H}_2\text{O}$ salt from the list of thorium sulphates.

† *Loc. cit.*, p. 202.

RESEARCHES ON THE METALS OF THE CERIUM GROUP.*

TREATISE I.

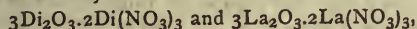
By P. SCHÖTTLANDER:

(Continued from p. 220).

3. Separation of Lanthanum and Didymium by the Oxide Process.

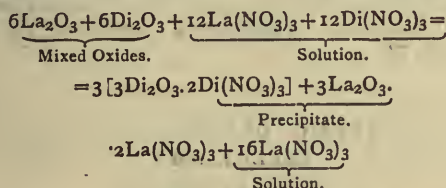
UNDER this name Auer von Welsbach describes a method of separation founded upon the formation of basic nitrates by the action of a mixture of the earths upon the neutral nitrate solution of the same mixture, and the much stronger basicity of lanthanum oxide as compared with the earths of the didymium and the yttrium group. In consequence of this stronger basicity lanthanum oxide remains predominantly in solution as a neutral nitrate, whilst the didymium and the still more feebly basic yttrium earths accumulate in the insoluble basic precipitate.

The basic precipitates obtained in this manner are essentially nothing else than hydrated compounds of the known basic didymium and lanthanum nitrates—

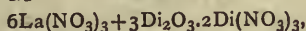


in which it is quite possible that in the first compound a part of the didymium may be replaced by lanthanum and inversely in the second a part of the lanthanum by didymium, which, in practice, does not come into consideration.

If we overlook this possibility the process may best be explained by a special case. If a solution contains equal molecular quantities of lanthanum and didymium we precipitate one half of the solution with oxalic acid, convert the oxalate into oxide, and treat this oxide, according to Auer's method, with the other half of the solution; the decomposition may then be represented by the following equation:—



Then come first in reaction $3\text{La}_2\text{O}_3$ of the mixed oxide with $8\text{Di}(\text{NO}_3)_3$ of the solution, and form—



upon which the residual oxides combine with corresponding quantities of the dissolved nitrates to form basic salts.

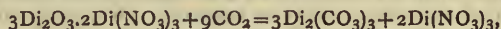
The results of numerous experiments (always approximately checked as regards the yield of oxides in the solution and the precipitate) always agreed completely with the relations demanded by these formulæ. Of course, the decomposition is never so complete as the above equation demands.

In carrying out the process it is necessary in the first place that the mixture of oxides obtained by igniting the oxalates should be heated as strongly as possible in a covered crucible, at least to bright redness for some time, so that it may lose all its carbonic acid, and it should be used before it can absorb fresh carbonic acid from the atmosphere. If this precaution is disregarded, it is sometimes quite incapable of acting on the solution of nitrate, even if all other precautions are duly observed. As regards the precipitation of the oxalate it is necessary to proceed exactly as was previously laid down for the precipitation of ceriferous solutions.

The solution to be treated with the oxide must be perfectly free from ammonium nitrate (the above-mentioned washing-waters can therefore serve only for precipitation with oxalic acid, whilst the first filtrates, free from cerium, may be used at once if sufficiently pure), and must of course contain no free nitric acid. Their concentration is preferably such that 1 grm. of oxides is dissolved in 8 c.c. of the liquid.

For instance, 100 grms. of oxide are first ground up dry in a mortar and then worked up to a quite uniform paste with the gradual addition of 100 c.c. of water; 800 c.c. of the solution of the nature above indicated are then added, and the whole is ground up most carefully. The reaction then generally sets in after a short time with a rise of temperature and a considerable thickening of the mass. Whether this takes place or not, the whole is transferred to a deep porcelain capsule, the mortar is rinsed out with 100 c.c. of water, and to complete the reaction the capsule is heated upon the water-bath for 30 to 60 minutes, stirring diligently and crushing any small lumps. The mixture is then allowed to cool a little, the pale, rose-coloured, paste-like mass is then transferred to a tall glass, the capsule is rinsed out with a minimum of tepid water, and the glass is then allowed to stand for 12 hours carefully covered. For extraction the mass is then made up to about 1400 c.c. by the addition of cold water, rendered uniform by means of prolonged and vigorous stirring, and allowed to stand for several days until perfectly clear.

As the basic nitrates eagerly attract carbonic acid, and thus didymium is re-dissolved—



the access of air should be excluded as far as possible. The solution is then decanted away from the precipitate as clear as possible; the precipitate is again stirred up with about 800 c.c. of water, allowed to settle, and the clear decanted liquid added to the former. It is not advisable to continue washing the precipitate, as in that case it no longer subsides. It is therefore poured upon a filter, the filtrate is returned to the funnel until it runs through clear, and is then permitted to drain, for which 24 hours are often scarcely sufficient.

Solution and precipitate are then further fractionated in a similar manner, the latter being first dissolved in nitric acid to a perfectly neutral solution, applying heat and adding the acid very slowly towards the last. In further fractionation it is advisable not each time to precipitate half the solution with oxalic acid, but in the lanthanum fractions to precipitate a smaller and smaller part in proportion as it becomes poorer in didymium; but in the didymium fractions, on the contrary, to throw down each time a larger and larger portion the more the didymium accumulates.

If, generally speaking, we wish to fractionate a fraction further, so that the proportion of the mixed oxides contained in the precipitate of basic nitrate to that found in the solution to be obtained = n , a portion of the fraction must be precipitated, which is calculated from the formula for the basic nitrate as—

$$\frac{3n}{4(n+1)}.$$

If this fraction reaches the value $\frac{3}{4}$, all the earths are separated out as basic nitrates.

As regards the concentration of the nitrate solution, which must be maintained in the subsequent fractionations, it may be remarked that in the lanthanum fractions we must not fall below a strength of 1 grm. oxide in 8.4 c.c. solution; whilst in the didymium fractions we must not exceed a strength of 1 grm. oxide in 7.5 c.c. of solution, without including the quantities of water above mentioned as required for grinding up the oxide and rinsing out the mortar.

(To be continued.)

DETERMINATION OF FERRIC OXIDE AND ALUMINA IN PHOSPHATES.

By R. JONES.

TEN grms. of the sample are dissolved in nitric acid and made up to 500 c.c., 50 c.c. of this solution (= 1 grm. of the original substance) are evaporated down to one-half in a beaker, mixed whilst still hot with 10 c.c. dilute sulphuric acid (1 : 5), stirred up, 150 c.c. of alcohol are added, and after again stirring allowed to stand for at least three hours. The calcium sulphate is collected upon a filter and washed with alcohol, filtering into an Erlenmeyer flask holding from 400 to 500 c.c. The washing is complete when the last ten drops, after dilution with an equal volume of water, are no longer reddened by a drop of methyl orange. A small Sprengel pump is very serviceable in washing.

If it is intended to weigh the calcium sulphate, it is laid whilst still moist in a platinum capsule, the filter is laid upon it, the alcohol is burnt away, and the mass ignited with a moderate flame until its weight is constant. The ignited calcium sulphate is not so hygroscopic as to interfere with working in an open capsule.

The alcohol is distilled off from the contents of the flask. It is contaminated with hydrochloric acid or nitric acid and their products of decomposition, and cannot be used again until it has been once more distilled over soda.

The residue from the distillation is washed into a beaker, slightly supersaturated with ammonia, and heated until all the ammonia has been expelled. This precaution is very necessary, as otherwise the precipitate of iron phosphate will be mixed with magnesia.

The residue is collected on a filter; the residues adhering to the glass are swept upon the filter by means of a glass rod tipped with caoutchouc and a jet of cold water. It is washed four times with boiling water poured out from the reversed washing-bottle in order not to stir up the precipitate. In this manner we always obtain clear filtrates. For still greater security a little ammonium nitrate may be added to the washing-water, which of course must not be acid. The precipitate is ignited and weighed.

The precipitate is assumed to consist of ferric and aluminium phosphate, exactly one-half of which is the joint weight of ferric oxide and alumina.

If the operator prefers to determine the ferric oxide and alumina as such, the mixed precipitate when ready for weighing may be dissolved in nitric acid, the phosphoric acid precipitated with the molybdic solution, filtered, and washed; the ferric hydroxide and alumina may be precipitated in the liquid by ammonia and weighed.—*Zeitsch. Anal. Chemie*, xxx., p. 742.

PHOTO-CHEMICAL NOTICES.

By P. ASKENASY and VICTOR MEYER.

IN a memoir on the slow combustion of gaseous mixtures, the authors mentioned that V. Meyer and Krause had exposed detonating gas for some months to the light of the sun in closed vessels without any formation of water being observed. No decisive value was ascribed to these experiments, as they were performed during the winter months. We have latterly repeated them, exposing bulbs of detonating gas to solar radiation uninterruptedly from May to October. But here also no change of volume was perceptible on opening the bulbs. It must be added that these results were obtained with the *dry* gaseous mixture. It remained therefore to be examined whether the behaviour of moist detonating gas would be similar.

If therefore a formation of water could not be effected by irradiation alone, it might possibly be produced if detonating gas was exposed to the sun's rays at atmospheric pressure and at a temperature immediately below

its point of ignition. For this purpose the intense light of a July sun was concentrated by a large concave mirror, and thrown downwards by means of a metallic plane mirror upon moist detonating gas kept at 60° in boiling stannous chloride. Ignition, however, was not observed.

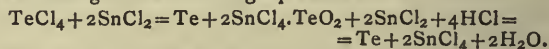
The authors further communicate some experiments undertaken to submit to a renewed test the accuracy of Draper's statements on the photo-chemical induction of chlorine. Draper maintained that a chlorine-detonating gas composed of chlorine and hydrogen previously irradiated possesses the property of combining to form hydrochloric acid even in the dark. Bunsen and Roscoe have rejected this observation as incorrect, showing that chlorine which had been passed outside the laboratory through a glass worm exposed to the rays of the sun, and was then mixed with hydrogen which had been similarly insulated, remained inactive on mixture with the latter in darkness. Against this method of experimentation the objection might be made that the chlorine had been exposed to the chemically active rays for too short a time; possibly a prolonged stage of induction might be required. The authors therefore repeated the experiments in a modified form, exposing chlorine in a long vessel containing 100.5 c.c., and capable of being closed at each end by means of glass cocks for three to four hours to the light of a July sun, the intensity of which was increased by a concave mirror. It was then shaded, the apparatus was placed in a vertical position, and 50 c.c. of hydrogen which had been similarly illuminated were introduced from above from a gas burette, whilst the displaced chlorine could escape at the lower aperture of the apparatus. The analysis of the gaseous mixture which was expelled after some time from the darkened space by means of pure carbonic acid and collected over soda-lye, showed that no hydrochloric acid had been formed, and the exact quantity of hydrogen taken had been recovered. Hence it is demonstrated that chlorine, even if irradiated intensely and for a long time, and hydrogen, similarly treated, do not combine with each other if at once introduced into darkness.—*Justus Liebig's Annalen der Chemie*, clxix., p. 72.

VOLUMETRIC DETERMINATION OF TELLURIUM.*

By BOHUSLAV BRAUNER.

First Method.

A HYDROCHLORIC solution of tellurium dioxide is reduced by stannous chloride, with separation of free tellurium and formation of stannic chloride. The transformation ensues according to the following equations:—



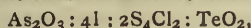
Brauner prepares the solution of stannous chloride by boiling about 80 grms. granulated tin with about 200 c.c. hydrochloric acid as long as hydrogen is evolved, decants off the liquid, adds to the 150 c.c. thus obtained 450 c.c. hydrochloric acid, and dilutes with water to 1 litre. The solution, which may be further diluted with water, according as larger or smaller quantities of tellurium have to be determined, is preserved in an atmosphere of carbon dioxide. Besides the solution of stannous chloride, there is required a solution of iodine containing per litre 7 grms. iodine and 10 grms. potassium iodide.

For determining tellurium he introduces the hydrochloric solution of tellurium into a measuring flask holding 100 c.c., and adds the solution of stannous chloride whilst applying heat. As long as the latter is not in excess, the liquid is turbid on account of finely pulverulent tellurium, but it clears at once, especially after ebullition,

* *Zeitschrift Anal. Chemie*.

as soon as stannous chloride is present in excess. After the experimentalist has convinced himself by adding a small quantity of stannous chloride that no further precipitation takes place, the flask is filled up to the mark with water which should preferably be free from air, and the air is expelled from the neck of the flask by the addition of a little sodium bicarbonate. The flask is then cooled down to the ordinary temperature, and whilst it is cooling the proportion between the iodine and the stannous chloride solutions is ascertained. When cold the flask is filled up to the mark, and in an aliquot portion of the clear supernatant liquid the excess of stannous chloride is determined by titration with iodine. If particles of tellurium still float in suspension in the liquid, it is first filtered through a dry folded filter, since in presence of hydrochloric acid finely divided tellurium slowly decolorises solution of iodine. The quantity of solution of iodine consumed is re-calculated for the entire volume (100 c.c.), and the corresponding quantity of stannous chloride is deducted from that used for precipitation.

In order to determine the effective value of the solution of stannous chloride, we may, on the one hand, ascertain the proportion of the iodine solution to a known quantity of arsenious acid, and, on the other hand, to the solution of stannous chloride. The following proportion shows the relation of the substances concerned:—



i.e., the same quantity of iodine which converts 198 parts (1 mol.) of arsenious acid into arsenic acid, shows the quantity of stannous chloride which reduces 159.6 parts (1 mol.) of tellurium dioxide.

The solution of stannous chloride may also be standardised for a weighed quantity of pure iodine or of pure tellurium dioxide.

The method is said by the author to give useful and approximately accurate results. The solution of stannous chloride is readily oxidised by the action of the air, and its strength decreases during the course of the experiment.

(To be continued).

THE CHEMICAL ANALYSIS OF ALUMINUM.*

By ALFRED E. HUNT, G. H. CLAPP, and J. O. HANDY.

(Concluded from p. 225).

Determination of Chromium in Chromium-Aluminum Alloy.

2 grms. of chromium-aluminum alloy are treated in a 5-inch porcelain dish, with about 50 c.c. of 10 per cent KOH solution. When action has slackened, the solution is boiled up, and finally filtered. The washed residue contains the chromium, together with some silicon, silica, iron, aluminum hydrate, and titanium, if present.

Burn off the filter paper in a porcelain crucible; transfer the residue to a large platinum crucible, and treat with 1 c.c. concentrated H_2SO_4 + 5 c.c. HF. Evaporate to SO_3 fumes; add 4 grms. bisulphate of potassium; cover the crucible and fuse for about 20 minutes at a low temperature. Finally heat to a high temperature over the blast-lamp to expel nearly all the free acid. Cool a little and add sufficient Na_2CO_3 to make alkaline; also a little KNO_3 , and fuse.

Dissolve in hot water and filter. Filtrate contains all the chromium as chromate, together with some alkali aluminate and silicate.

Decompose the latter by warming the solution with NH_4Cl , and filter.

Reduce the chromium in the filtrate, by sodium sulphite or sulphurous acid, and precipitate the chromium as hydroxide by means of ammonia, as usual.

Re-dissolve the $\text{Cr}_2\text{H}_6\text{O}_6$ in HCl; dilute and re-precipitate with ammonia, to free from alkali, taking the usual precautions as to washing free from chlorides in each case.

Weigh as Cr_2O_3 .

If the intermediate fusion with bisulphate is omitted, some chromium will not be oxidised.

Method of Analyses of Titanium-Aluminum.

2 grms. of the alloy in a porcelain evaporating dish (5 inches in diameter and covered by a watch-glass) are dissolved by gradual addition of 50 c.c. of "potash solution" (100 grms. KOH in one litre distilled water). Boil for 10 minutes to insure complete solution. Dilute with distilled water to about 125 c.c. Boil up and filter as quickly as possible, washing ten times with boiling water. This filtration separates the iron and titanium quite completely from aluminum. Burn off the residue in a porcelain crucible. Crush it in an agate mortar, and mix with about 8 grms. (6 grms. first, then 2 grms. later) of pure bisulphate of potassium. Fuse in a thin-walled platinum crucible of about 40 c.c. capacity. The cover of the crucible should fit well.

During the first 15 minutes, the crucible should be on a platinum wire triangle over a small flame of a Bunsen burner. The burner flame should be protected from draughts by a sheet-iron chimney, and the flame at first should just touch the crucible bottom. At intervals of 5 minutes remove the cover, carefully invert it (without losing the drop of KHSO_4), and place it on a clean stone surface. Then give the contents a rotating motion, holding the crucible firmly in the tongs. At the end of 15 minutes, turn up the light till the lower one-fourth of the crucible is red hot; agitate frequently as before. In ten minutes more, turn on flame full and heat for five minutes, with shaking. Cool, add 2 grms. more KHSO_4 , and gradually bring to a homogeneous fusion, but do not heat long enough to drive off much free SO_3 .

Pour out the liquid fusion into a warmed and dry platinum dish; after the cake cools it will not adhere to the dish. Place it together with the crucible and cover in a 200 c.c. beaker. Add 150 c.c. of water; heat to and keep at 40°C ., with frequent stirring, until all soluble matter is dissolved. Filter, rejecting the residue, if ignition and treatment with HF show it to be only SiO_2 . If it contains anything more, fuse with KHSO_4 again.

Estimation of Titanium.

The filtrate contains all the TiO_2 and Fe_2O_3 . Add dilute NH_4OH to slight precipitation not re-dissolved by stirring. Add dilute (1 to 3) H_2SO_4 until this precipitate just re-dissolves. Add 4 drops of concentrated H_2SO_4 to the solution, dilute to 250 c.c., and saturate with sulphurous acid gas. Heat slowly to boiling, and boil gently for three-quarters of an hour. Add a little strong SO_2 water occasionally to keep the iron in the ferrous state. Filter through double-washed filters, and wash with hot water. Ignite in porcelain crucible over the blast-lamp.

Weight of $\text{TiO}_2 \times 0.60 = \text{Ti}$.

Estimation of Iron.

In the filtrate from the TiO_2 , the Fe is oxidised, precipitated by NH_4OH , filtered and washed, re-dissolved in HCl, and titrated with bichromate. Do not weigh the Fe_2O_3 and Al_2O_3 as precipitated. Attempts to titrate the iron in the sulphate solution occasionally give results which are not accurate.

Estimation of Silicon in Titanium-Aluminum Alloy.

Silicon is estimated just as usual, except that we use a little more HCl (20 c.c.) in re-dissolving after evaporation with H_2SO_4 . Under these conditions, no TiO_2 remains with the silica, although it is best to test it, always, with HF and H_2SO_4 .

* Journal of Analytica and Applied Chemistry.

A REVISION OF THE ATOMIC WEIGHT
OF COPPER.*

By THEODORE WILLIAM RICHARDS.†

CONTENTS:—Introduction.—Balance and Weights.—I. Analysis of Cupric Sulphate; Materials; Description, Three Series; Cause of the Deficiency; Atomic Weight of Sulphur; Atomic Weight of Copper.—II. Synthesis of Cupric Sulphate.—III. Analysis of Cupric Oxide; Tests for Impurities; Determination of Occluded Gases.—IV. Upon Typical Copper.—V. Summary of Results.

INTRODUCTION.

It will be remembered that recent investigation upon the atomic weight of copper has pointed toward the existence of a value for that constant very different from the one indicated by earlier determinations. During the winter of 1886–87 a number of experiments (*Proc. Amer. Acad. Arts Sci.*, xxii., 342) were made in this laboratory upon the replacement of silver from solutions of argentic nitrate by means of metallic copper; and during the following winter these were supported by similar series (*Ibid.*, xxiii., 177; *Fres. Zeitschr.*, xxviii., 392) involving material from different sources. The consistent verdict of all these experiments indicated a considerably higher atomic weight than that which had previously been accepted; but although the new method seemed to be in every way satisfactory, the presumption must nevertheless remain in favour of the older value until the presentation of more evidence against it. Accordingly, another method of determination was devised, and the two distinct but concordant series of results obtained by this method fully confirmed the higher value. The aspect of the case was now wholly changed,—it presented two series of coincidences, of which one must necessarily be due to chance alone; and in such a case certainty can be reached only through a complete and intelligent reconciliation of the conflicting evidence. A careful examination of the possible sources of inaccuracy involved in all recent analyses failed to reveal the probability of a constant error greater than two or three units in the second decimal place. Therefore a complete examination of the older work seemed imperative, and the object of the present paper is to describe such a revision.

A brief review of earlier determinations is given in the first paper of the present series, but for the sake of convenient reference a complete summary is repeated below. On account of the present uncertainty with regard to the ratio of oxygen to hydrogen, the standard to which the figures in the following table are referred is the arbitrary one, O=16; and this standard has been adopted throughout the present paper.

Atomic Weight of Copper.

O = 16.000.

Berzelius, 1828 (<i>Pogg. Ann.</i> , viii., 182), from CuO	Cu = 63.29
Erdmann and Marchand, 1844 (<i>J. Pr. Chem.</i> , xxxi., 391), from CuO	53.47
Dumas, 1859 (<i>Ann. Chim. Phys.</i> , [3], lv., 129, 198), from CuO and Cu ₂ S (?)	63.50
Millon and Comaille, 1863 (<i>Compt. Rend.</i> , lvii., 147; <i>Fres. Zeitschr.</i> , ii., 474), from CuO	63.12
Hampe, 1874, from CuO	63.34
" " CuSO ₄ , (<i>Fres. Zeitschr.</i> , xiii., 352; xvi., 458)	63.32
Baumbach, 1883 (<i>Compt. Rend.</i> , xcvi., 854, 906), from CuSO ₄	63.47

* Contributions from the Chemical Laboratory of Harvard College from the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

† For a previous paper on this subject, by the same author, see *CHEM. NEWS*, vol. lxiii., p. 20.

Shaw, 1886, through electrolytic equivalent	63.48
" corrected (<i>Phil. Mag.</i> , [5], xxiii., 138)	63.51
Richards, 1887, 1888 (<i>Proc. Amer. Acad. Arts Sci.</i> , xxii., 342; xxiii., 177), by relation to silver	63.60
Richards, 1890 (<i>Ibid.</i> , xxv., 195), from cupric bromide (two series)	63.61

The low value obtained by Hampe has been until recently universally accepted, because of the care employed in his analytical work, and the agreement between his results. Hence the present discussion will be confined almost entirely to the two substances which formed the bases of his operations.

The following values for the atomic weights of various elements entering into the present investigation will be assumed throughout the paper.

Oxygen =	16.000	Hydrogen =	1.008
Barium =	137.10	Silver =	107.930
Bromine =	79.955	Sodium =	23.053
Carbon =	12.002	Sulphur =	32.060

BALANCE AND WEIGHTS.

The balance used in the work to be described was made with especial care by Henry Troemner, of Philadelphia, and was procured particularly for the present research. The beam and pans are composed of aluminium, and all the remaining metal work is plated with gold. By raising the centre of gravity, the pointer may be made to swing with great constancy as much as eight divisions of the scale for one-tenth of a milligram; but since this degree of sensibility is far beyond the range of accuracy obtainable even in atomic weight investigation, the balance was usually adjusted so that the pointer moved ten divisions for a milligram. A reasonable increase in load altered this relation but slightly. The balance was kept in a small closet lined with curtains, and was protected as much as possible from changes in temperature. The air of the case was dried by means of potassic hydroxide and sulphuric acid, and large dishes of the former substance were kept in the closet outside.

The standard weights have already been described (*Proc. Amer. Acad. Arts Sci.*, xxv., 196). They were carefully rubbed with chamois skin and again compared before the present work. The slight corrections, which scarcely differed at all from those previously found, were applied to each weighing.

A double rider attachment upon the balance made the method of weighing by substitution accurate and easy; and accordingly this method was invariably adopted, except in the first series of experiments upon cupric sulphate. In general, the vessel to be weighed was carefully tared with an adjusted set of common gilded weights, and the vibrations of the pointer were noted. After the removal of the vessel, standard weights were added to the left-hand pan until the same condition of equilibrium was reached. The vessel was then once more substituted for these weights, and any slight change of centre point was of course manifest at once. In the rare cases when such slight change appeared, the weights and vessel were alternately substituted for each other until constancy was reached. In the case of hygroscopic substances, the already ascertained weights were first placed upon each scale pan, then the vessel was quickly removed from the desiccator and substituted for the standard weights, and, finally, the latter were again put in place.

All desiccators were allowed to remain in the closet with the balance three or four hours before the weighing, and objects were often weighed on successive days, to furnish assurance of constancy. In every case the barometer and thermometer were read, and any correction due to change of relative buoyancy amounting to more than the fiftieth of a milligram was applied to the result. With large vessels an invariable slight loss of weight, amounting

Sometimes as much as one-twentieth of a milligram, was noticed after the object had remained for some time upon the balance pan. The loss may have been due to the replacement of the perfectly dry air from the desiccator by the less completely dried air of the balance case. Possible error from this source was avoided by the employment of uniform conditions suited to the particular substance in hand.

All weighings were of course reduced to the vacuum standard by calculation from the specific gravities of the substances and weights involved (*Proc. Amer. Acad. Arts Sci.*, xxv., 1896. Specific gravity of brass = 8.3). Through the great kindness of Professor Mendenhall, of Washington, two of the laboratory's ten-grm. weights (one of brass and one of platinum) have been compared as carefully as possible with the standards of the Washington Bureau of Weights and Measures. Five comparisons of the Sartorius ten-grm. weight with these gave the following results for its value in vacuum:—

		Grms.
1891.		
Feb. 4.	By comparison with the brass weight	10.00025
Mar. 4.	" " platinum "	10.00025
Mar. 14.	" " " "	10.00026
June 12.	" " " "	10.00026
June 12.	" " " "	10.00024
Average		10.00025

The third and fifth of these comparisons were made with the balance in the condition of greatest sensibility, while the others were made exactly in the usual manner. It is not pretended, however, that all the weighings which follow have probable errors so small as these. The results are nevertheless an excellent gauge of efficiency of the balance, especially since the observations were made at widely varying temperatures and pressures. The correction involved, applying in the same proportion to all weighings, has been omitted from the following figures; but any weight given below may of course readily be reduced to the Washington standard by multiplication with the factor 1.000025.

(To be continued).

OBITUARY.

THE LATE PROFESSOR A. W. VON HOFMANN.

THE scientific world has received a painful shock by the death of August Wilhelm von Hofmann, which took place the 5th inst. The deceased was beyond question one of the foremost chemists of the time; widely and honourably known, both for his brilliant researches in some of the most interesting departments of organic chemistry, and for his successful career as a teacher of his science both in Germany and England.

Like so many other young chemists of the second quarter of the century, Hofmann received his training at the University of Giessen, under Liebig, and then took up the study of the coal-tar bases and their metamorphoses. In 1848, at Liebig's recommendation, he was appointed Professor at the Royal College of Chemistry in London, then just called into being. His career here was eminently successful. He was found to have imbibed the spirit of his master Liebig, and the laboratory of the Royal College became, under his guidance, a school of chemistry similar in its efficiency to that of Giessen. Not a few of the most eminent English chemists were trained under his directions, and we are justified in saying that they one and all retain a grateful recollection of his patience, his perseverance, and his kindly interest in their progress. We had previously had in Britain chemists of the highest merit, but in the Royal College of Chemistry we had for the first time a school of chemistry on a level with the requirements of the day. Hofmann

remained in London till 1864, having been in the meantime appointed (1855) to the Wardenship of the Royal Mint. In 1864 he was called to the chemical professorship at the University of Bonn, and in 1865 he was appointed to the chemical chair at the University of Berlin. Here he renewed his activity. Besides continuing his researches on the coal-tar bases, especially rosaniline, he distinguished himself by his success as a teacher and by his efficiency as one of the foremost scientific advisers of the German Government whenever chemical questions were concerned. He took an active part in the organisation of the German Chemical Society, and was its President at the time of his death.

Recognition of his merits was not wanting. In 1851 he was elected a Fellow of the Royal Society, and in 1854 he became a recipient of the Royal Medal in especial consideration of his "Researches on the Molecular Constitution of Organic Bases." In 1875 he received from the Royal Society the Copley Medal—the "blue ribbon" of science. He has been President of the Chemical Society of London, and was up to his death one of its vice-presidents.

Although Hofmann felt it a duty to accept the positions offered him in his native country, he always looked back with pleasure to his sojourn in London and to the numerous and attached friends he had gained here. In both countries he will be deeply and widely regretted.

NOTICES OF BOOKS.

Elements of Materia Medica and Therapeutics; Including the whole of the remedies of the British Pharmacopoeia of 1885 and its Appendix of 1890. By C. E. ARMAND SEMPLE, M.B., M.R.C.P. London: Longmans, Green, and Co.

By far the greater portion of this work can be appreciated only by the medical and pharmaceutical world. It is interesting to note that certain vegetable matters which enjoy a high reputation among the general public here figure less prominently. Thus bael fruit is pronounced "probably not superior to some other vegetable astrin-gents." Even the wonder-working chirata or chiretta—as it is represented by certain vendors of proprietary nostrums—is here described as "acting exactly like gentian."

A painful fact is the uncertainty which seems to prevail concerning the properties of many drugs. Again and again we read: "It is said to act"; "it is said to be antidotal, &c."

Many of the illustrations are calculated to be exceedingly useful for the identification of medicinal plants, but we fail to see the reason for figures of a pig, a sheep, or an ox.

As far as chemical compounds are concerned, it is very unsatisfactory that medical writers still employ a distinct nomenclature—distinct from that employed for scientific purposes, and from the industrial terminology.

Blowpipe Analysis. By J. LANDAUER. Authorised English Edition, by JAMES TAYLOR, B.Sc. Second Edition; Revised and Enlarged, 1892. London: Macmillan and Co.

The appearance of this book we may regard as a sign that more attention is being turned to the use of the blowpipe in inorganic analysis. On the value of this little instrument, both for preliminary testing and often as the only available guide for the prospector, the mining engineer, &c., when obliged to work in situations where the appliances of a regular laboratory are not available, it is needless to enlarge.

The author treats in succession of apparatus and reagents, and of the operations in blowpipe analysis, with

an appendix on Bunsen's flame reactions. An important improvement here is the use of the spectroscopic in the not un-frequent case that several flame colouring elements occur together. Browning's direct-vision pocket spectroscopic is recommended as most serviceable for blowpipe work, and it will certainly not form any appreciable addition in bulk or weight to the outfit of a travelling explorer.

Chapter III. gives directions for special examinations for certain elements in combination.

In Chapter IV. we have two systematic courses of examination for compound inorganic substances, Landauer's own and Egleston's.

In conclusion there are a condensed view of blowpipe reactions and a tabular view of the behaviour before the blowpipe of the alkalis, earths, and metallic oxides, whether alone or with reagents.

This little work deserves the highest recommendation for its clearness, comprehensiveness, and portability.

A Summer School of Art and Science. Summer Meeting, Edinburgh. (*Vacation Studies*). Sixth Session, August 1st to 31st. University Hall, Edinburgh, Easter, 1892.

WE have not often met with a prospectus which called up in our mind such sympathetic interest as does the present. The idea of utilising a part of the long university vacations for studies of a peripatetic and open-air character is not indeed novel. At some of the German polytechnic schools the curricula include excursions to places of geological or botanical interest, as well as to interesting industrial establishments, mines, smelting and refining furnaces, tinctorial works, &c. And at some of the universities a party of students during vacation will sometimes get up among themselves an exploring expedition, in which they proceed as if investigating an unknown country. These excursions, though sometimes accompanied by a professor, are perfectly unofficial.

"Summer schools" have also been organised in the United States, though one of these gatherings, held at Concord a few years back, rendered itself unpleasantly conspicuous by its anti-evolutionary, or rather anti-scientific, utterances.

But Edinburgh may claim the credit of having taken up these scattered threads and woven them into a complete tissue. The movement seems to have attracted attention abroad since last year. The French Minister of Public Instruction deputed two eminent *savants*, Prof. Espinas, of Bordeaux, and Dr. Henri de Varigny, of Paris, to investigate and report on the scheme. This year it is hoped that lectures will be delivered by Professor Haeckel, of Jena, and Dr. de Varigny, of Paris.

We cannot give a summary of the intended proceedings without reprinting a considerable part of the prospectus. But there are not a few points which we must notice with satisfaction.

Thus political economy will be taught not by men contemptuously ignorant of the physical and natural sciences, but by such men as Prof. Geddes. The principle of Evolution will be applied in the courses of literature and anthropology. Thus in the latter department the infant will be considered as parallel to the anthropoid, and the child to the savage. The criminal will be viewed as a case of arrested development or of reversion.

In Art, "the study of landscape and animal life is definitely associated with the school of natural science, and that of (human) figure with anthropology and history, the student thus working for the artist, and the artist for the student."

Another laudable feature is the extent to which mere book-learning or verbalism is to be superseded or at least modified by actual familiarity with the objects or processes to be explained. Many of the lessons will be given in the museums (scientific and industrial), at the Granton marine station, in mines, and in places of geological interest, which are certainly not lacking in the Edinburgh district.

It is impossible to examine this prospectus without sharing in the hopes of the promoters that a step is being taken which will lead to the solution of the pressing educational problems of the present age.

The fee for the entire course is £3 3s. Gentlemen may board in University Hall, Mound Place, at 21s. to 26s. weekly; whilst ladies may be accommodated at the same rates at University Hall, Riddle's Court.

Throughout the entire prospectus there is no reference to any "syllabus" or examination. The student is evidently called upon not to cram his memory, but to cultivate his faculties of observation and to assimilate methods. On the title-page of this pamphlet there is a design of birds flying, but they are evidently not Strassburg geese.

Agricultural Research Association for the North-Eastern Counties of Scotland. New Organisation, 1891.

THIS report by Mr. Thomas Jamieson contains no little interesting information. We are told in the introduction, and with too much truth, that "the tendency of the age is to regard as an essential feature of success a speedy return for outlay." This feeling, the author justly urges, should be resisted as fatal to success. Sound research, whether its ultimate object be theoretical or practical, cannot be hurried.

It is found that experimental stations should be not merely enclosed, but even covered over with a bird-proof wire netting. Some of the plots had to be twice re-sown, as whole drills had been systematically cleared of their plants. It is a question not taken up by the author, but we might ask whether the purely zoöphagous birds, such, e.g., as the wag-tails, could not be encouraged at the expense of the phytophagous species?

As a complete manure Mr. Jamieson recognises one supplying nitrogen, phosphorus, and potash. Hence he does not agree with M. Ville in placing lime in the same rank with the three above-mentioned substances.

He still holds that manures containing sulphuric acid, such as dissolved bones, superphosphate, &c., is the main cause of the "club-root" disease in turnips. As a mixture for turnips he recommends 1 part each of steamed bone-flour, of nitrate of soda, and nitrate of potash, 4 parts ground coprolite, and 6 parts basic slag. We are somewhat sceptical as to the value of undissolved coprolite. Slag, it appears, is now adulterated with the Redonda phosphate, which is of marvellously little—if any—value as plant food.

In an interesting inquiry on the function of the root-hairs of plants, it is suggested that plants take up their solid food in the solid form through the air-root apertures.

A Practical Introduction to Chemistry. Intended to give a Practical Acquaintance with the Elementary Facts and Principles of Chemistry. By W. A. SHENSTONE, Lecturer on Chemistry in Clifton College, 1887. London: Rivingtons. Small 8vo., pp. 108.

THIS little work is said to be a "new edition," and to have appeared in 1887, though it is only now sent for notice. The author has previously done such good service by the production of his "Methods of Glass-Blowing" that we cannot do other than regret that he should have spent his time in adding one more to the existing swarm of elementary treatises on chemistry.

We are weary of asking ourselves, that such books are more plentiful in Britain than in other civilised countries, how is it that publishers can always be found for them? and other painful questions. It is certain that the crop can bear no definite proportion to the seed sown, otherwise we should be richer than any of our neighbours in chemical discoverers, inventors, and industrialists. Such, we need scarcely say, is by no means the case. Is it possible that these books are an indirect product of the dominant examinational system? The author's introductory chapter contains much that is decidedly valuable.

Sanders's Question Compend, No. 2. Essentials of Bacteriology; Being a Concise and Systematic Introduction to the Study of Micro-organisms for the Use of Students and Practitioners. By M. V. BALL, M.D. With 77 Illustrations, some in colours. Small 8vo., Pp. 159. Philadelphia: W. B. Saunders. 1891.

THIS work is, as it professes, a concise introduction to the study of micro-organisms,—those at least belonging to the vegetable world. Its appearance is a proof of the increased attention which the physician and the sanitarian are now paying to the study of those ultra-microscopic beings some of which rank among our most formidable enemies. As far as the subject matter is concerned the author has performed his task well, very few statements being found to which exception may be fairly taken. It may, perhaps, be submitted that the dependence of Beggiatoa on sulphur is not brought into sufficient prominence. This unlovely plant is, indeed, sometimes found "where the remains of organic life are decomposing," but only where such remains contain a sufficiency of sulphur.

The author's language offers ample room for improvement. We do not notice the frequent errors, clerical or typographical, in proper names except where they may occasion confusion. Thus we find mention of the "Chamberland" filter and also of that of "Chamberlain." It is possible for a student to suppose that we have here to do with two different filters. It might also be doubted whether Van Tiegham and Van Tiegham were or were not identical. In reality they are both incorrect versions of one name, Van Tieghem. We must decidedly object to such words as "aerobins" and "anaerobins." The correct English words would, we submit, have been "aerobians" and "anaerobians." The expression "aniline oil" is very needless; aniline when existing in a free and non-modified state is of course a liquid of a somewhat oily appearance, but nothing save needless complication is gained by always keeping this fact before the reader. Certain abbreviations are doubtful, e.g., "tr. iodine," also "6 gtt. of turpentine" and "5 gtt. of safranin (Bismark-brown)". We hope that Bismark-brown is not here given as a synonym for safranin.

Not a few passages in the work will expose the writer to vituperation from the opponents of physiological experimentation, who will dub him an "artist in filth and torture." However, he will not be the only man who has been maligned for seeking to extend the dominion of Science.

The work before us will, we hope, induce many students to enter upon a deeper investigation of the "infinitely little."

The Pharmaceutical Review, Vol. I., Nos. 1, 2, and 3. THIS new journal, though ably edited and written, contains very little which can legitimately come under our notice. It is a business organ, having for its principal function to maintain the rights of the pharmacist in America as against his foes, the "cutter," the "jobber," the fussy meddler, and, above all, the quack. Whether he has also, like his British colleagues, to make head against the encroachments of the monopolist draper we do not learn. The new review and the body it advocates have our best wishes.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 17, April 25, 1892.

Means of Artificially Occasioning Rain.—M. Faye. —The means proposed are fires or explosions. The author concludes that there is a radical distinction be-

tween ascending currents of hot air and tornados, and regards the hopes entertained of producing rain at will as illusory.

Analysis of a Chromiferous Clay from Brazil.—A. Terreil.—Chromium sesquioxide is present only to the extent of 1.69 per cent.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xvii., No. 1.

Densimetric Determination of Phosphorus in Cast Irons.—E. Metz.—A modification of the process published by R. Popper in the *Zeit. für Anal. Chemie*, vol. xvi., p. 157, and vol. xviii., p. 14. The weight of a precipitate is determined on the densimetric method, according to the following equation—

$$\alpha = \frac{S}{S-s}(G-g).$$

where S is the specific gravity of the precipitate, s the specific gravity of the solution in which the precipitate is present, G the weight of the picnometer containing the solution and the entire precipitate, g the weight of the picnometer containing the solution alone, and α the weight of the precipitate to be determined. The value S is supposed to be known, G and g are found by weighing, and s by calculation. For the specific gravity of four determinations the author gives as a mean 3.252. He objects to the gravimetric method on the grounds that the precipitate of ammonium phospho-molybdate is not absolutely insoluble in the liquids used for washing, and that the drying the precipitate affects its constitution.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 7.

Action of Acetic Anhydride upon Dimethylaniline.—F. Reverdin and Ch. de la Harpe.—Acetic acid reacts upon dimethylaniline at common temperatures and in presence of air, occasioning the formation of tetramethyldiamidodiphenylmethane.

Action of Secondary Capryl Iodide upon Trimethylamine in an Aqueous Solution and in Equimolecular Proportion in the Cold. Formation of Caprylene and Trimethylamine Hydriodate.—H. and A. Malbot.—In the cold there are formed only two products, caprylene and trimethylamine hydriodate, whilst in heat there are formed in addition dimethylcaprylamine and tetramethylammonium iodide.

Nitrised Butyltoluene- and Butylxylene-sulphonic Acids.—E. Noeling.—It is a general fact that the sulphonic acids of strongly odoriferous bodies are absolutely scentless. Of this we have numerous examples in all classes of bodies. Thus benzene, naphthalene, nitrobenzene, aniline, naphthylamine, quinoline, benzaldehyd, phenol, naphthol, biiodophenol, have all very decided odours. Their sulpho-conjugated acids in a pure state are absolutely inodorous.

Assay of Ores of Antimony.—Ad. Carnot.—Already inserted.

Reduction of the Nitrates of the Aromatic Amines and their Transformation into Chlorinated Hydrocarbons.—M. Prudhomme and C. Rabaul.—This paper does not admit of useful abstraction.

Novel Synthesis of Tartaric Acid.—P. Genviesse.—The author treats glyoxylic acid with zinc-powder in presence of acetic acid diluted with its own weight of water, firstly at common temperatures and then in the water-bath. The filtered liquid is treated with potassium carbonate, and after the precipitate has been filtered off, with calcium chloride. The white precipitate formed has all the characters of calcium racemate.

Determination of Potassa.—F. Jean and M. Trillot.—Instead of sodium formiate the authors propose to use a solution of formic aldehyd.

MISCELLANEOUS.

Institute of Chemistry.—A Conference of the Members of the Institute will be held at the Rooms of the Chemical Society, Burlington House, at 3 p.m., on Monday, May 16. The subject for discussion will be: "The Present Regulations with Respect to the Admission of Fellows and Associates to the Institute."

Congress of German Naturalists and Physicians.—This body, the oldest of the itinerating associations for the advancement of science, will hold its 65th meeting at Nuernberg, from September 12th to 16th. Memoirs, &c., to be produced should be announced before the end of May, as the general invitations will be sent out in the beginning of July.—*Chemiker Zeitung*.

Researches on the Adherence of the Various Cupriforous Dressings used to Combat Fungoid Diseases in Plants.—Aimé Girard. — In heavy rains certain of the preparations used to combat the potato-disease and the mildew of the vines have been washed away and have in consequence proved ineffectual. The most easily displaced among these preparations was the well-known "Bordeaux broth" (copper sulphate 2 kilos., slacked lime, weighed as quicklime, 2 kilos., water 100 litres). The most resistant are the "Burgundian broth" (copper sulphate 2 kilos., soda-crystals 3 kilos., water 100 litres), the formula of Michael Perret (copper sulphate 2 kilos., lime 2 kilos., treacle 2 kilos., water 100 litres), and a mixture which has been successfully employed at Montpellier, consisting of bibasic copper acetate stirred up in water (verdigris 1 kilo. 600 grms., water 100 litres).—*Bull. Soc. d'Encouragement pour l'Industrie Nationale*, viii., No. 75.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Spontaneous Breaking of Glass.—On the night of Friday, the 29th of April, about 10 o'clock, a remarkable thing happened here. An ordinary cut crystal tumbler containing a little drinking water, standing on the sideboard, cracked with a very loud report. The conditions in the room were nominal, but the tumbler was near a window looking to the north, and at the time there was a brilliant display of aurora borealis. It would be very interesting to know the cause of this accident, and I shall be pleased to give any of your curious readers any other information.—B. S.

Respiration of Plants and Animals.—(Reply to I. L.).—The apparent contradiction pointed out by your correspondent "I. L." is very clearly explained in Bennett's Edition of Thome's "Botany." The misunderstanding arises from a loose application of terms. In the process of assimilation plants absorb carbon dioxide and decompose it with the elimination of oxygen, the carbon being retained and built up into the plant tissues. In the process of respiration plants absorb oxygen from the atmosphere, not, however, in order to assimilate it, but, on the contrary, in order to decompose the substances contained in the plant, to deprive them of at least a part of their carbon, the products of this action being then exhaled as carbon dioxide. Respiration is therefore a process diametrically opposed to the process of assimilation. To describe them under the same name is as incorrect as if we were to speak of an animal inhaling its food.—HENRY B. WOODALL.

Respiration in Plants and Animals.—(Reply to I. L.).—I am unable at the moment to give the name of any book which accounts for the apparent contradiction mentioned in last week's issue of the *CHEMICAL NEWS* by your querist "I. L.," but the following is the received explanation. All living organisms, whether animal or vegetable, as a necessary result of those processes of oxidation without which life is impossible must exhale carbonic anhydride as a final product. This is a respiratory action, and in the case of animals and of plants containing no chlorophyll (e.g., most fungi) this elimination of carbonic anhydride is easily demonstrated. When, however, we turn to the chlorophyll-bearing plants, we find this action masked by another, not respiratory, but assimilative. These plants have, by means of their chlorophyll, the power in the light of absorbing carbonic anhydride, and with the aid of the elements of water-producing carbohydrates such as cellulose, starch, and sugar, with the elimination of oxygen. Disregarding intermediate reactions, this equation is typical, $6\text{CO}_2 + 10\text{H}_2\text{O} = \text{C}_6\text{H}_{10}\text{O}_5 + 6\text{O}_2$. In the light this assimilative action so preponderates over the other, the respiratory, as to mask it completely, but, in the absence of light, the chlorophyll

becomes inactive, and then in chlorophyll-bearing plants, as the assimilative process has ceased, the exhalation of carbonic anhydride may be demonstrated as in the case of animals and fungi.—A. PERCY HOSKINS, F.I.C.

MEETINGS FOR THE WEEK.

- MONDAY, 16th.—Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Industries," by Percy F. Frankland, F.R.S. (Cantor Lectures).
TUESDAY, 17th.—Institute of Civil Engineers, 8.
— Pathological, 8.30. (Anniversary).
— Society of Arts, 8. "Mud, a Material for Architecture in Persia and the East," by William Simpson, R.I.
— Royal Institution, 3. "Photography in the Colours of Nature," by Frederick E. Ives.
WEDNESDAY, 18th.—Society of Arts, 8. "Colour Blindness," by Capt. W. de W. Abney, F.R.S.
— Microscopical, 8.
— Meteorological, 7.
— Pharmaceutical, 11 a.m. (Anniversary).
THURSDAY, 19th.—Royal, 4.30.
— Royal Institution, 3. "The Chemistry of Gases," by Prof. Dewar, F.R.S.
— Institute of Electrical Engineers, 8.
— Society of Arts, 4.30. "The Administration of the Imperial Census of 1891 in India," by Jervoise A. Baines, I.C.S.
— Chemical, 8. "Magnetic Rotation of some Acetyl Derivatives," by W. H. Perkin, F.R.S. "Studies in Isomeric Change, No. IV.—Halogen Derivatives of Quinone, Part I," by A. R. Ling. "Note on Diastatic Action," by E. R. Moritz T. A. Glendinning. "Formation of the Hydrocarbon $\text{C}_{18}\text{H}_{12}$ from Phenylpropionic Acid," by Dr. Kipping.
FRIDAY, 20th.—Royal Institution, 9. "Electro-Metallurgy," by J. Wilson Swan, M.A., F.C.S.
— Quekett Club, 8.
SATURDAY, 21st.—Royal Institution, 3. "J. S. Bach's Chamber Music," by E. Dannreuther.

THIS DAY IS PUBLISHED.

FARMYARD MANURE:

ITS NATURE, COMPOSITION, AND TREATMENT.

By C. M. AIKMAN, M.A., B.Sc., F.R.S.E., F.I.C., F.C.S., Lecturer on Agricultural Chemistry, West of Scotland Technical College; Examiner in Chemistry, University of Glasgow, &c.

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PATENTS, DESIGNS, & TRADE MARKS ACT,
1883 TO 1888.

NOTICE IS HEREBY GIVEN, that

THE FARBWERKE VOMALS MEISTER LUCIUS AND BRÜNING, of Höchst-am-Main, Empire Germany, have APPLIED for LEAVE to FURTHER AMEND the SPECIFICATION of the Letters Patent, No. 43 of 1886, granted to Charles Denton Abel for "Improvements in the production of colouring matters or dyestuffs."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents, issued on the 4th May, 1892. Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment, within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,
Comptroller-General.

ABEL AND IMRAY,
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THE CHEMICAL NEWS.

VOL. LXV., No. 1695.

THE ESTIMATION OF NITROGEN.

By VINCENT EDWARDS, F.O.S.

HAVING to constantly use Kjeldahl's process for the estimation of nitrogen in manures and numerous substances, I have attempted by various modifications to render the method more accurate and rapid, and as the following notes may be of interest I venture to publish them.

It is well known that many substances used as artificial fertilisers contain nitrogen in three distinct forms, viz., organic, ammoniacal, and oxides of nitrogen; and for the estimation of the first two the ordinary process answers very well, but when the substance contains nitro-oxides the results are unsatisfactory.

It occurred to me that it might be possible to combine the ordinary Kjeldahl process with a method by which nitrates are analysed. The principle of the method to which I refer is the reducing action of nascent hydrogen on a nitrate in solution. Though to all appearance this method is easily carried out, the practical difficulties are great; it is a somewhat delicate operation to heat for a considerable time a glass flask containing a quantity of zinc and iron filings without risk of fracture; I therefore thought that by using a flask of iron containing granulated zinc, or rather zinc grains, the process might be rendered much safer, and at one and the same operation all nitrogen in whatever form might be estimated.

To begin with I made experiments carrying out the ordinary Kjeldahl process in a flask of thin iron with a coating of tin such as are used for oil, &c. Having procured some substances the nitrogen in which was known,—to give an example, in a manure which contained 11.00 per cent of ammonia,—I found 11.37 per cent, a result which is excessive; but on making three estimations in blank, I found that on an average a deduction of 0.00176 gram of ammonia might be made from the result; this being done the final result is 11.08 per cent of ammonia, which is within the limit of error.

The small quantity of ammonia is not contained in the reagents, but is formed by the action of the moist oxide of iron in the flask on the air, the flask being always moist after an experiment.

Among advantages of iron flasks are that heat can be applied strongly at once, and the analysis is finished sooner; also, that after starting the operation requires little or no looking after till the conclusion. To be sure the distillate is not always quite clear, but a plug of cotton-wool in the bulb tube which joins the flask as usual to the condenser in a measure averts this; nor are the iron flasks permanent, but for that matter few things are in a laboratory or elsewhere, and the cost is a trifle.

For substances which contain small quantities of nitrates this method is very successful, and a minute though important amount of nitrogen is thus rescued from being passed over. In the analysis of soils, for instance, comparatively large quantities can be treated this way, and greater accuracy obtained. I may state that there is no novelty here except in the application, as Arabian chemists many centuries ago used flasks of metal, copper for instance.

It is well to use the same quantity of sulphuric acid in each preliminary digestion, say 20 c.c., also a known sufficiency of strong soda solution, making the acid liquid dilute before adding to the flask 20 c.c. of a 40 per cent solution of potassium sulphide as usual. If the distillate is not clear it can be filtered through an English paper,

but this is hardly ever necessary. Three or four blank distillations, the lapse of one night between each, will give an average quantity of ammonia to deduct in each case, and indeed this peculiarity is rather of service than otherwise, as it makes the titration more certain in cases where the amount of ammonia is very small.

Lawes Works, Barking, May 13, 1892.

ACTION OF AMMONIC CITRATE ON HIGH GRADE ALUMINIC PHOSPHATE.*

By H. A. HUSTON.

IN the latter part of July a sample of high grade aluminic phosphate was submitted to me for analysis. The results desired were the amounts of total and of "available" phosphoric acid present. As the material was quite different from the ordinary fertiliser stock, a series of experiments were made to determine the effects of varying the conditions used in the official method for available. Three methods for determining total phosphoric acid were used, and gave closely agreeing results.

The material was stated to be anhydrous phosphate of aluminum, which had been calcined. It was found to contain 45.46 per cent of phosphoric acid and 7.25 per cent of silica. There was no soluble phosphoric acid present in the sample. The work on available phosphoric acid was made by using in all cases 100 c.c. of the official citrate solution. In the fourth series solid citric acid and ammonic hydrate were added. The results appear in the following tables:—

SERIES I.—Effect of Increasing the Time of Digestion.

(Amount taken, 2 grms.; temperature, 65° C.; 100 c.c. citrate solution).

Time of digestion.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
One-half hour	21.24	46.75
One hour	31.70	67.53
Two hours	36.92	81.10
Four "	40.80	89.67
Six "	41.00	90.11
Ten "	42.70	93.85

SERIES II.—Effect of Changing the Temperature at which the Digestion was Conducted.

(Amount taken, 2 grms.; time, thirty minutes; 100 c.c. citrate solution).

Temperature.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
40° C.	2.18	4.79
50° C.	5.52	12.10
65° C.	21.24	46.75
75° C.	32.90	72.30
85° C.	39.52	87.90

SERIES III.—Effect of Changing the Amount of Phosphate Taken.

(Temperature, 65° C.; time, thirty minutes; 100 c.c. citrate solution).

Amount of phosphate taken.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
1/2 gm.	16.80	36.9
1 "	18.26	40.1
2 grms.	21.24	46.7
3 "	23.22	51.0
5 "	24.66	54.2
10 "	28.64	62.9

* From the *Proceedings of the Seventh Annual Convention of the Association of Official Agricultural Chemists, Washington.*

SERIES IV.—Effect of Making the Citrate Solution Acid or Alkaline.

(Amount taken, 2 grms.; time, thirty minutes; 100 c.c. citrate solution).

Amount of acid or alkali added to the solution.	Per cent dissolved.	Fraction of total phosphoric acid dissolved.
2 grms. citric acid	17'21	37'21
1 gm. " "	18'26	39'49
0'75 gm. citric acid	17'84	38'58
0'50 " "	19'98	43'20
0'10 " "	21'08	45'60
0'05 " "	21'14	45'70
Neutral solution	21'32	46'10
Ammonia enough to neutralise 0'05 gm. citric acid	23'44	50'70
Ammonia enough to neutralise 0'10 gm. citric acid	24'38	52'70
Ammonia enough to neutralise 0'50 gm. citric acid	26'02	56'30
Ammonia enough to neutralise 1'00 gm. citric acid	30'78	66'60

The only set of the above results that seems to require any special comment is Series III., where the results are rather unexpected. The work in this direction will be continued in order to find out whether the peculiar effect is due to the fact that the digestion is stopped before the solution is complete, or whether a solution of aluminic phosphate in ammoniac citrate really has a greater solvent power than the original solution of ammoniac citrate.

The commercial importance of this matter will appear from the following:—Suppose the high grade phosphate is used in making up goods to the extent of one-fourth their weight. Then there should be 5'31 per cent of available derived from the aluminic phosphate. But if the results in series are correct there would appear on analysis only 4'20 per cent of available from this source.

The matter is also of considerable interest from a purely scientific standpoint.

VOLUMETRIC DETERMINATION OF
TELLURIUM.*

By BOHUSLAV BRAUNER.

(Concluded from p. 235).

Second Method.

THE author attempted to find a further volumetric determination of tellurium upon the oxidation of tellurous acid to telluric acid by means of chromic acid or potassium bichromate. In these experiments a hydrochloric solution of tellurous acid diluted with water was mixed with a solution of potassium bichromate in excess, and after some time the excess of bichromate was titrated back with an acidified solution of ammonium ferrous sulphate.

The oxidation of the tellurous acid is the more complete the greater the volume of the solution of chromate originally added, the larger the quantity of hydrochloric acid present, and the more prolonged the action. The oxidation is effected very slowly, and only approximates on completion after an hour. The main reaction is accompanied by a disturbing secondary reaction, which is recognised by a slight odour of chlorine or of ozone. A decomposition of the solution containing hydrochloric, chromic, and telluric acids takes place at the expense of a small quantity of chromic acid, whereby the results are rendered rather too high. The method possesses, therefore, theoretical possibility, but only a slight practical value.

Third Method.

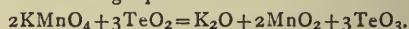
Attempts to determine tellurium iodometrically by the action of solution of iodine upon alkaline solutions of tellurous acid (alkaline tellurites), proved failures, as the oxidation of tellurous acid by iodine is only gradual. A complete oxidation may certainly be effected by prolonged action with the aid of heat, but the excess of the iodine added cannot be accurately determined.

Fourth Method.

Since the behaviour of tellurous acid with chromic acid in a hydrochloric solution, and with iodine in an alkaline solution, shows that the oxidation to telluric acid proceeds but slowly, the author tried the use of a more energetic oxidising agent, permanganate.

Attempts to determine tellurous acid in a hydrochloric or sulphuric solution by titration with solution of permanganate gave no satisfactory results, since in the reaction along with the formation of manganic chloride or sulphate there always took place a liberation of chlorine or ozoniferous oxygen. The inevitable development of oxygen and the excessive consumption of solution of permanganate thus occasioned led always to false values. Useful results could be obtained by this method only if an especial correction is introduced, or if the solution of permanganate is standardised under the same conditions with a weighed quantity of tellurium dioxide.

Decidedly better results were obtained on titrating tellurous acid with permanganate in an alkaline solution, as here no escape of free oxygen or ozone is to be observed. The oxidation of tellurous acid ensues according to the following equation—



In reality there is formed an alkaline tellurate, and perhaps a compound of telluric acid and manganese.

In the practical execution of this process decinormal potassium permanganate is added to the alkaline solution of tellurium dioxide until the former distinctly predominates. The solution is then mixed with an excess of dilute sulphuric acid, and so much decinormal oxalic acid is added that its volume corresponds to about half that of the permanganate added. On applying heat, the higher oxides of manganese dissolve, whilst the liquid becomes completely colourless, and may be titrated with solution of permanganate at 60° in the known manner.

The titration is effected in an alkaline solution without the escape of oxygen, but on the addition of sulphuric acid a faint but distinct odour of ozone is apparent. The excessive consumption of permanganate thus occasioned does not on an average amount to more than 0'35 per cent. If decinormal oxalic acid is used for standardising the solution of permanganate the factor must be diminished by this small quantity. If the permanganate is standardised with pure tellurous acid this correction is, of course, dispensed with.

If tellurium dioxide has to be determined in a hydrochloric solution either the first method may be used or the following process. The hydrochloric solution is evaporated down on the water-bath with a little sulphuric acid, and the highly concentrated solution is heated for some time on the sand-bath in order to expel the last traces of hydrochloric acid. There is no reason to fear any appreciable loss of tellurium tetrachloride by volatilisation. The dilute solution is then supersaturated with pure sodium hydroxide, and titrated with permanganate as above described.

According to the author, the determination of tellurium with permanganate is both more exact and expeditious than all previous methods.

A Soluble Naphtholic Compound.—M. Stackler.—The compound obtained, for which the name asaprol is proposed, seems to be serviceable for destroying the microbes of cholera, typhoid, and splenic fever.—*Comptes Rendus*, cxiv., No. 18.

* *Zeitschrift Anal. Chemie*.

RESEARCHES ON THE METALS OF THE
CERIUM GROUP.*

TREATISE I.

By P. SCHÖTTLANDER.

(Continued from p. 233).

THE process of fractionation followed with the 808 grms. of earths free from cerium can be seen in the following conspectus. The approximate quantity of oxides is appended in most fractions.

The colour of the highly concentrated solutions of the nitrates prepared from the eight fractions obtained was:— In the fraction Di III. a_1 , which must contain all the earths of the feeblest basicity, a rather dark dirty violet-rose; in the intermediate fractions, a rather lighter and purer violet-rose; in fraction La III. b_2 , almost colourless by daylight, but by gaslight a very pale rose; finally, in fraction La III. b , a greenish yellow by daylight, but a dirty rose by gaslight. In this fraction, therefore, the oxide process had already effected a perceptible splitting up of didymium into its components.

On account of the very tedious and unpleasant work with the above-mentioned, quite amorphous, and rather bulky precipitates of nitrates, no further attempts were made to obtain a salt of lanthanum perfectly free from didymium, and a salt of didymium perfectly free from lanthanum, by this method. The fractions La II. a , Di III. b_2 , and Di V. a were, instead, united as almost of equal value, and the six fractions of the total material thus obtained were submitted to the process of crystallising their double nitrates, as it will be briefly explained in the next section.

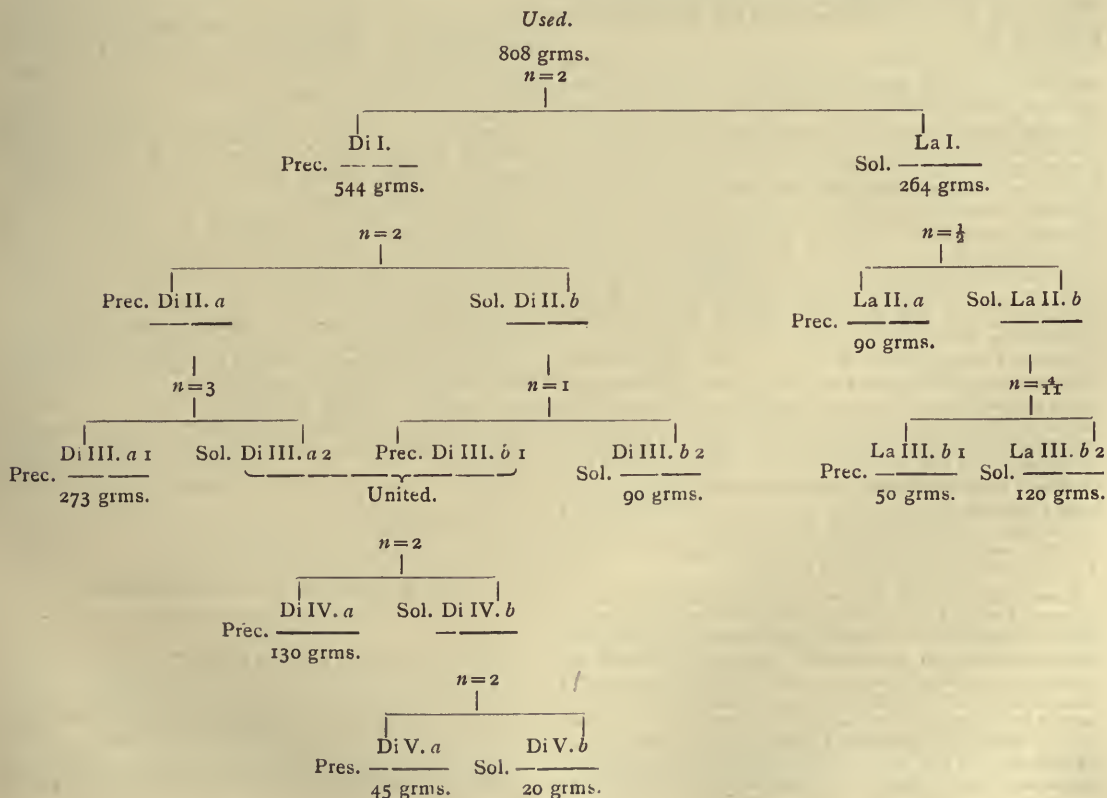
* *Berichte der Deutsch. Chem. Gesel*

4. Preparation of a Pure Lanthanum Salt and Partial Re-solution of Didymium into its Components by the Crystallisation of the Double Ammonium Nitrates.

The principles and the practical execution of this process have been described by Auer von Welsbach with such completeness that we need merely mention in addition a few stratagems which are adapted to expedite the very tedious operation.

The crystallisation may be easily performed in rather deep porcelain capsules of suitable size, in which the saline solution, acidulated with nitric acid, set upon a wire net, and heated with a small flame until minute crystals become visible upon the surface, which do not disappear upon stirring after the removal of the flame. These tiny crystals are not the double salt sought for,

$R(NO_3)_3 \cdot 2NH_4 \cdot NO_3 \cdot 4H_2O$, which appears in fine massive monosymmetric prisms and tables, but probably a compound poorer in water. When the chief quantity of the lanthanum salt has been fractionated out, it is important that the six or eight fractions to be obtained from each portion of salt should be approximately equal in quantity. In order to effect this without weighings, we add to the hot liquid a little cold water from the washing-bottle, stir up, and place a drop on a watch-glass. We then add by means of forceps with platinum points a trace of the crystallised salt of an approximately equivalent fraction, and stir up with one of the points of the forceps. If too much water had not been added, crystallisation begins immediately in the drop, and is completed in a few seconds. If the entire drop congeals to a paste, a little more water is cautiously dropped into the capsule, and the experiment is repeated in another part of the watch-glass. In this manner with a little practice it is easy, from the quantity of crystals obtained in the drop, to estimate approximately



the quantity obtainable from the entire solution. After the solution has been duly concentrated, some of the crystalline paste on the watch-glass (which may be inspissated at pleasure by heating the watch-glass and crystallising anew) is added to the liquid, which has been allowed to cool in the air, at its margin in small quantities until the formation of crystals is observed; the rest of the crystalline paste is then distributed at two other places of the capsule, covered over, and left to itself from six to twelve hours according to the proportion of saline matter. A more prolonged crystallisation extending to twenty-four hours is requisite only at the beginning when larger quantities of saline matter are concerned. It often happens in the course of the operation that the impurities present, calcium and ferric nitrate, &c., and an excess of ammonium nitrate, accumulate to such an extent that the liquid can no longer be brought to crystallise. The fraction must then be precipitated with oxalic acid, and the oxalate be re-converted into the double salt.

As regards the formation of the simple series of crystals, the above material was treated as follows:—After the saline mass taken in hand was resolved into six to eight portions of crystals of the first series, each of the latter was again severed into five to six portions, so that there resulted some forty fractions. Of these, all those were mixed together which at an approximately equal degree of concentration showed no difference in the tone of their colour if compared in glass vessels of similar form. Thus the number of fractions was reduced to some twenty. Of these, the even numbers were brought to crystallise by crystallising out about half of the saline mass which they held in solution, and then each time adding the mother-liquor to the succeeding but the crystals to the foregoing fraction, after the former has been rinsed in the capsule with a little concentrated nitric acid. The crystals of fraction 2 were thus put to fraction 1, the mother-liquor and the washings to fraction 3; the crystals from fraction 4 to fraction 3, the mother-liquor and the washing acid to fraction 5, &c.

The ten (about) fractions thus obtained were called the second series. By again dividing each of these portions into five or six deposits of crystals, and mixing together the solutions of the same colour, we again obtained some twenty of the latter, which, by using the above halving-process, yielded about ten fractions of the third series, &c. These fractions in each series were then characterised by Roman numerals, the several fractions obtained from splitting up fraction I. as I_1, I_2, I_3 ; those from II. as II_1, II_2, II_3 When towards the end of the process differences of colour were no longer perceptible, fraction I_3 was united to II_1 , fraction I_4 with II_2 , fraction I_5 with II_3 and III_1 , fraction II_4 with III_2 , fraction II_5 with III_3 and IV_1 , &c.

Of the saline portions obtained by the oxide process, that produced by the union of three of the mean fractions is separated by a number of crystallisations into portions which have experienced about the same degree of separation as those above characterised, as La III. b_1 , La III. b_2 , Di IV. a , and Di V. b , and the latter are then united successively with the equivalent fractions of that series. The crystallisation was continued with this material to the eighth and tenth series, and thereby almost all the lanthanum was eliminated mostly as a slightly greenish salt. The didymium fractions were set aside.

Lastly, the didymium main fraction, Di III. a_1 , which contained 270 grms. of earths almost free from lanthanum, after conversion into the ammonium double salt, was taken in hand. As, according to Auer von Welsbach, the scission of didymium is more easily effected in presence of lanthanum, this fraction was again mixed with a solution of lanthanum salt of a decided greenish colour containing about 70 grms. of oxide, and the mixture was fractionated by four series of crystallisations. After obtaining the fourth series the lanthanum salt, which had been chiefly recovered in the first fractions, was again

distributed among the intermediate and the last fractions, the addition of lanthanum then ceasing.

As it was chiefly important to establish the behaviour of all the earths present in the raw material (excepting the cerium oxides) towards the crystallisation process of the double ammonium nitrates, the separation of the feebly basic earths of the yttrium group by the oxide process was intentionally omitted. On the other hand, the last syrupy and uncrystallisable mother-liquor of the above-mentioned fourth series was precipitated with oxalic acid before the addition of lanthanum, the oxalate was converted into oxide, dissolved in hydrochloric acid, and the solution precipitated with finely powdered potassium sulphate in excess. The precipitate was carefully washed with a saturated solution of potassium sulphate, and decomposed by boiling with a large excess of soda-lye. The flesh-coloured and rather compact hydroxide after washing with hot water was again dissolved in hydrochloric acid, and on precipitation the oxalic acid, &c., yielded 51.6 grms. of earths, to which, after conversion into the ammonium double salt, about 30 grms. lanthanum oxide were added in the form of the greenish double salt. Now crystals were obtained of the normal form, but only in thin lamellae, which retained the glutinous mother-liquor very obstinately. The crystals were therefore drained, washed with a little concentrated nitric acid, and again further fractionated along with the foregoing fraction, whilst the mother-liquors which contained much lanthanum were set aside as the final fraction.

(To be continued.)

ON THE VALUE AND THE VARIATIONS OF THE CHEMICAL VALENCIES.

By CARLO EMILIO CARBONELLI.

THIS memoir is reprinted from the *Transactions* of the Ligustic Society of Natural Science (*Società Ligustica di Scienze Naturali*). In it the author seeks to establish the following propositions.

Each element has a characteristic tendency, common in general to the entire Mendeleeffian group to which it belongs, to consist in a fixed number of special atomic groupings which have a different stability according to the nature of the substance.

Compounds may be generated by substitution, by addition, and by substitution along with addition. There exist special groups (radicles) which act as regards their valency like isolated atoms.

Hydroxile exists only in acids and in bodies which, though neutral, like alcohol and H_2O , possess hydrogen capable of substitution. Only the hydrogen of hydroxyl is substitutable by metals; H_2O is, however, a monobasic acid. The anhydrides are not saturated compounds, since they are acids deprived of water.

To form compounds by substitution is a property of the non-metals characterised by the complexity of their molecule.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 237).

I. THE ANALYSIS OF CUPRIC SULPHATE.

THE only published analyses of cupric sulphate which have had for their object the determination of the atomic weight of copper are those previously mentioned. Hampe

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

has very clearly described two extremely concordant electrolytic determinations of the copper contained in the so-called anhydrous salt. The greatest care had been taken to separate minute traces of metallic impurities from the preparation, which had been dried at 250° C.; but apparently it was not realised that for the purpose in hand the retention of a trace of water by the salt was a much more serious possible cause of error than any other. Baubigny's analyses are less fully described, so that it is less easy to judge of their value. A different method, the conversion of cupric sulphate into the oxide by heat, was adopted for these experiments. The result was very different from that obtained by Hampe, but was more nearly accurate, because complicated with a less serious combination of constant errors.

The entire reconciliation of all these results, not only with each other, but also with the more recent analyses, involved the complete analysis and synthesis of cupric sulphate. A somewhat detailed account of the various operations is given below. Many of the less important points are necessarily omitted on account of the already too great accumulation of material, and many relations between the figures can be worked out by those whom they may interest. It is to be hoped that the effort to spare the overburdened literature of to-day any unnecessary additions may not have interfered with the clearness of the description. The first three series of experiments upon the analysis of cupric sulphate constituted a study of the effect of progressive refinement, and the first of the three perhaps hardly deserves a place in a paper on atomic weights. Unless otherwise stated, the data are given in full.

Materials used in the Analysis.

Cupric Sulphate.—The substance used in the first series of experiments was partly prepared from very pure copper remaining from the cupric bromide research, and partly from other sources. It was perfectly neutral and reasonably pure. For the second and third series 400 grms. of the so-called "chemically pure" cupric sulphate of commerce were dissolved in a very large amount of water, and the solution was twice successively treated with a very small amount of potassic hydroxide in dilute solution; the mixture being occasionally shaken and allowed to stand each time for a week before decanting the clear supernatant liquid. One quarter of a gm. of ammoniac bromide was added to this liquid; and after standing two weeks the solution was carefully filtered, evaporated to very small bulk in a porcelain dish, and again filtered from the deposited basic salt. The finely divided crystals obtained from this solution by agitation and cooling with ice were drained with a reverse filter (see *Proc. Amer. Acad. Arts Sci.*, xii., 124), re-dissolved in hot water, and repeatedly re-crystallised in platinum vessels. The first three mother liquors were rejected, but the later ones were all combined. After three more re-crystallisations the substance contained in these mother liquors was dissolved in cold water and allowed to crystallise by slow evaporation in pure air. The preparation thus made was used in the second series of analyses.

The crystals obtained by eight successive crystallisations in platinum vessels were dissolved in cold water, and the salt was slowly re-crystallised over sulphuric acid in a vacuum. The substance thus obtained was dissolved in water which had been distilled in a platinum retort, and after standing six days the perfectly clear solution was again brought to crystallisation in a vacuum. These crystals were dried in a platinum dish over partially dehydrated cupric sulphate, and were used for the third series of experiments. The neutrality of each of these preparations was determined as nearly as possible by means of methyl orange, after the manner described in the *Proc. Amer. Acad. Arts Sci.*, xxv., p. 201.

Sodic Carbonate.—As sodic carbonate formed one of the chief bases for the determination of the sulphuric acid, its manufacture in a pure state was a matter of great impor-

tance. From the "chemically pure" material of commerce one may easily procure by five re-crystallisations a material which gives no colouration with ammoniac sulphhydrate, nor, after neutralisation, with potassic sulphocyanide.* Sodic sulphate and chloride are even more readily separated than traces of iron.

Three separate preparations of sodic carbonate were used in the course of the work. For the first series of comparatively crude experiments the solution of ordinary "chemically pure" material, which almost invariably contains a perceptible amount of finely divided solid matter, was after filtration twice re-crystallised in a platinum dish. It was subsequently found advantageous to prevent the clogging of the filter by two or three preliminary re-crystallisations, in the course of which most of the solid matter finds its way into the mother liquor.

The second sample of sodic carbonate was re-crystallised six times after filtration. The vessels, rod, and reverse filter were all of platinum, and water was used which had been distilled in a platinum retort.

Besides all these precautions, several additional ones were taken in the preparation of the purest sample of sodic carbonate designed for the third series. The water used had been distilled four times: first alone, next over potassic permanganate, then over acid potassic sulphate, and finally in a platinum still without the addition of foreign matter. Every precaution was taken to exclude dust and acid fumes, and the sodic carbonate was re-crystallised ten times after filtration. The salt prepared in this way gives an absolutely odourless warm concentrated solution. The second and third samples gave essentially identical results. Each of the three preparations was pure snow-white, whether fused or unfused; each gave a perfectly clear and colourless solution with water; and not even the first gave the least test for hydrochloric or sulphuric acid.

On the other hand, as Stas has already indicated, the most elaborate precautions are unable to free sodic carbonate wholly from traces of silica and a basic oxide, which is probably alumina. The former impurity was determined in the usual manner. The alumina and silica were determined together in new portions of the salt by exact neutralisation with hydrochloric or sulphuric acids, ignition of the evaporated product, and weighing of the insoluble residue. Phenolphthalein was used to determine the neutral point, and hence the insoluble bases present were necessarily precipitated. It is needless to state that the operations were conducted in platinum vessels. Neglecting two determinations which were vitiated by known impurity, the weight of total residue obtained varied from 0.15 to 0.41 m.grm., while the weight of sodic carbonate taken varied from 1.02 to 3.06 grms. The average of twenty determinations showed about thirteen parts of impurity to exist in 100,000 parts of the salt. Silica constituted about 40 per cent of this impurity. The third specimen did not differ essentially from the second on these averages. Owing to the slight solubility of silica in sodic chloride solutions,† the observed amount of this impurity may be slightly too low, but for the present purpose the correction is unimportant. The filter papers used in this part of the investigation left upon ignition an ash of 0.00004 gm.

(To be continued).

On an Ethylnitroacetone and an Acetylnitroacetone, derivatives of the Camphosphophenols.—P. Caze-neuve.—The composition given for ethylnitroacetone is $C_9H_{10}(C_2H_5)(NO_2)O$. That for acetylnitroacetone is $C_9H_{10}(C_2H_3O)(NO_2)O$.—*Comptes Rendus*, cxiv., No. 18.

* Stas appears once or twice to have had more difficulty in accomplishing this result. At other times his experience seems to have coincided with that described above. Compare Aronstein's translation (1867), pp. 112, 270, with 275.

† Stas, Aronstein's translation, p. 270. In this place the correction is applied to sodic chloride, but not to the nitrate formed from it.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 21st, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. J. W. Alcock, Central Brewery, 45, Mott Street, Birmingham; Frederick Whiteley, B.A., 20, Dunkerley Street, Oldham.

The following paper was read :—

9. "*Masrite, a New Egyptian Mineral, and the possible Occurrence of a New Element therein.*" By H. DROOP RICHMOND and HUSSEIN OFF.

The mineral in question is a variety of fibrous alum, sent to the Khedival Laboratory at Cairo by S. E. Johnson Pacha. From 1 to nearly 4 per cent of cobalt was found in different samples. This being the first occasion on which cobalt has been met with in Egypt, the authors were led to inquire whether the blue colour used in paintings on Egyptian monuments contained that element; They were unable to detect it, however, in the samples they obtained, which owed their colour to compounds of copper and iron.

The mineral is principally interesting on account of the presence in it of a minute quantity of a substance having properties apparently unlike those of any known element, which the authors provisionally term *masrium*, from the Arabic name for Egypt.

From an analysis of the oxalate, on the assumption that it is a bivalent element, the atomic weight of "*masrium*" is calculated to be 228; and the authors point out that there is a vacant place in the periodic system in the glucinum calcium group for an element having the weight 225. In many of its properties "*masrium*" resembles glucinum, and the oxalate is analogous to that of calcium.

Masrite has the composition—

$(Al, Fe)_2O_3 \cdot (Ms, Mn, Co, Fe)O_4 \cdot SO_3 \cdot 20OH_2$, the following being the results of the analysis of one of the samples examined :—

Water	40.35
Insoluble matter	2.61
Alumina	10.62
Ferric oxide	1.63
Masric "	0.20
Manganous oxide	2.56
Cobaltous "	1.02
Ferrous "	4.23
Sulphuric "	36.78
	100.00

Ordinary Meeting, May 5th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Percy Targett Adams, Ophthalmic Hospital, Maidstone; Charles Bayliss, Selby Park, near Birmingham; Arthur Sanderson Bleckly, Thelwall Lea, near Warrington; Henry Coudong, H.M. Mint, Bombay, India; Herbert Entwistle, Crosshill Terrace, 476, Padiham Road, Bromley; John Fenton Newall, Marple, and 8, Market Place, Manchester; Charles James Norris, Skipton Grammar School; Ernest Heber Smith, 54, Cambrian View, Chester.

The following were duly elected Fellows of the Society:—Alexander Barratt; Reginald Busby Brown; George Fitz Brown; Frederick William George Blyth; Meredith Wynter Blyth; Arthur Carey; Frank Comyns, B.A.; Joseph Davies; George Price Dodds; Hudson Donald-

son; Walter William Duffield; Walter N. Edwards; Henry Ellison; James Fraser, F.R.S.S.A.; Haridas Gorgari, M.A.; Harold F. Hills; Henry Leonard Hinnel, A.M.I.C.E.; John Theodore Hewitt; John H. B. Jenkins; Hubert Edward Lindley; Albert Augustus Lintern, B.Sc.; George Harry Major; William James McKerrrow; Ernest E. Milnes; Cresacre George Moore, B.A.; Albert Morris; Joseph Charles Mulrenan; John Northing; Albert Ernest Richardsen; Reginald Edensor Stanley Richardson; John Meadows Smith; William Herbert Stables, B.A.; James Stenhouse; George de Roos Thomson; Arthur Trobridge; Arthur Holt Tuer; Thomas Shortridge Tweedie; Cyprian A. Warren; George Isaac James Wells, F.I.C.; Lawrence John de Whalley, B.Sc.

The following extract was read from a letter to Sir Henry Roscoe, written by Prof. Kühne, of Heidelberg, at the request of Professor Bunsen, who is seriously unwell.

Heidelberg, April 21, 1892.

"Bunsen sent for me this morning and commissioned me to ask you to express to the Chemical Society his most sincere and hearty thanks for the much valued Address, the contents of which have gratified him highly.

"As he has always regarded the foundation of the Society, which he well remembers, as an important event of great scientific promise, so now he looks back with particular satisfaction on the fact that he has been a Fellow since its establishment, and that he has been permitted to take part in the work of the Society, especially during its earlier years, by the publication in its *Transactions* of many of his investigations. The allusion of this circumstance in the Address, and the appreciative recognition of his scientific labours which it contains, have been to him especially grateful. To his deep regret he finds himself unable to write, or indeed, to exert any continued mental effort, and he is therefore obliged to deny himself the pleasure of personally expressing his thanks, but begs that you will ask the Society to accept them in this form."

The following papers were read :—

10. "*The Existence of Two Acetaldoximes.*" By WYNDHAM R. DUNSTAN and T. S. DYMOND. (First Notice.)

Acetaldoxime, $CH_3CH:NOH$, has hitherto been regarded as a liquid capable of existing only in one form, attempts to obtain evidence of the existence of an isomeride having failed; last summer, however, the authors observed that it could be crystallised. The crystals, which are acicular and often several inches long, melt at 46.5° (corr.); when they are melted and the resulting liquid is heated to $100-150^\circ$, no decomposition occurs, the boiling point (114.5° , corr.) remaining unaltered, but on cooling, it does not crystallise until nearly 35° below the freezing point of the original liquid, that is at about 12° (corr.). On standing at the ordinary temperature the freezing-point of this liquid gradually rises until it reaches 46.5° . The crystals which separate from the liquid at 12° are found to be the original substance melting at 46.5° .

It thus seems probable that acetaldoxime can exist in two isomeric, or possibly polymeric, forms. The authors propose to designate the modification melting at 46.5° *a-acetaldoxime*, whilst that which is liquid at ordinary temperatures they provisionally name *β -acetaldoxime*.

During the past six months they have been investigating the physical and chemical properties of these two modifications with the view to discovering other differences between them, but these experiments are not yet completed. This preliminary account is now given, as they wish to complete the investigation, Franchimont having recently announced that he has observed the crystallisation of acetaldoxime, and is looking for evidence of an isomeride.

Acetaldoxime may be readily prepared by the action of hydroxylamine chlorhydrate on aldehyd-ammonia; the

calculated quantities of these substances are mixed together, and the acetaldoxime extracted from the mixture with ether. The ethereal solution is then carefully distilled in the usual manner. An almost theoretical yield is obtained.

11. "Sulphonic Acids Derived from Anisoils (No. I.)" By G. T. MOODY, D.Sc.

In the course of experiments made in the Central Institution Laboratory to elucidate the manner in which isomeric sulphonic acids are formed from phenols, and especially to determine the character of the influence of the OH group, the author has had occasion to study the action of sulphonating agents on methyl and ethyl phenyl ethers. He finds that, contrary to the statement of Kekulé (*Zeit. fur Chemie*, 1867, 20), and Opl and Lippmann (*Zeit. fur Chemie*, 1869, 470), anisoil and phenetol afford only parasulphonic acids.

Kahlbaum's pure preparations were employed in the experiments. The anisoil was dried over sodium and carefully distilled. It boiled constantly at 153° (uncorr.), but the first and last portions were collected apart. On shaking 50 grms. of the ether with an equal volume of sulphuric acid at the ordinary temperature, it readily dissolved, heat being evolved; on adding the solution to water, however, part of the anisoil was liberated, showing that, as in the case of phenol, an intermediate compound is formed before the sulphonic acid. The anisoil thus set free was shaken with a further quantity of sulphuric acid at 80°, when complete sulphonation occurred. The products were separately converted into calcium salt, which, on evaporation of the aqueous solution, was obtained in beautiful, long, shining needles, containing 4 molecular proportions of water. The sodium salt crystallises in short, slender needles, which fall to powder on exposure to the air; the potassium salt was obtained in small scales, very soluble in water. Further quantities of the same calcium salt were obtained on fractional crystallisation of the mother-liquors, but there was no indication of any other product being formed. The sulphochloride crystallises from petroleum spirit in elongated hexagonal plates melting at 40.5°; the sulphonamide melts at 108°. Sulphonation of anisoil with chlorosulphonic acid, either warm or in the cold, gave rise to the same sulphonic acid, and no other was obtained.

Phenetol, like anisoil, on sulphonation either with sulphuric acid or with chlorosulphonic acid, either warm or in the cold, gave rise to only the para-acid, the barium salt of which has been described by Lippmann. The sodium salt forms well-characterised, flat, slender, and somewhat brittle needles, and is anhydrous; the sulphochloride crystallises from light petroleum in flat, monosymmetric plates, which melt at 39°, the sulphonamide forming well-defined needles which melt at 150°.

12. "The Formation of Trithionate by the Action of Iodine on a Mixture of Sulphite and Thiosulphate." By W. SPRING.

In his paper on the "Investigation of the Change proceeding in an Acidified Solution of Sodium Thiosulphate," Colefax (*Chem. Soc. Trans.*, 1892, 181) credits me with having said that trithionate of sodium is produced when iodine acts on a mixture of sodium sulphite and thiosulphate, and further denies that this is the case. ("Spring's statement is not true.")

As already pointed out (*Chem. Zeitung*, xvi., 146), I never performed the experiment described by Colefax; I made use (*Bull. de l'Acad. Roy. de Belgique*, [2], xxxviii., 1874) of potassium, and not of sodium salts; in the abstract of my paper published in the *Transactions of the German Chemical Society* (vii., 1161, 1874, and not 1873, 1108, as stated by Mr. Colefax), it is true that sodium salts are spoken of, but this is an error which is due to the fact that the proofs were not submitted to me for correction. A perusal of my original paper in the *Bull. de l'Acad. Roy. de Belgique* (*loc. cit.*) will at once convince the reader of this fact.

The difference in the behaviour of potassium and sodium salts, arising from the greater instability of the polythionates of sodium, an instability which I had already pointed out in 1874, is very striking. Hence it would appear that the strictures made by Colefax are beside the question.

However, in order to avoid any misunderstanding in future, I trust that I may be permitted to draw attention to the following facts.

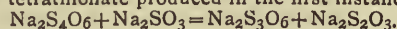
Colefax has performed his experiments under modified conditions, not only as regards the substitution of sodium for potassium salts, but also as to the proportion of iodine which he has made use of. In my experiments with potassium salts, the full proportion of iodine was not used, but a much smaller quantity. The equation $K_2SO_3 + K_2S_2O_3 + I_2 = K_2S_3O_6 + 2KI$ requires less iodine than would be necessary to oxidise the sulphite to sulphate, and the hyposulphite to tetrathionate of sodium.

I have thought it desirable to ascertain whether a suitable modification of the quantity of iodine used would lead to the production of trithionate, notwithstanding the great instability of this compound, as in the case of my experiments with potassium salts, in 1874. This will explain my delay in contradicting the imputations made by Colefax.

50.4 grms. of sodium sulphite, together with 49.6 grms. of sodium thiosulphate, were dissolved in iced water so as to avoid the decomposition of the trithionate in the subsequent action. To this solution 25.4 grms. of iodine, that is, half the quantity required for complete oxidation, were added in small portions at a time. The solution was then mixed with alcohol (95°). After a few days, the well-cooled alcoholic liquid deposited a small quantity of crystals containing sodium trithionate, which was identified by suitable tests. The principal product of the action, however, was sodium sulphate.

Nevertheless, I do not contend that the formation of trithionate takes place in accordance with the equation $Na_2S_2O_3 + Na_2SO_3 + I_2 = Na_2S_3O_6 + 2NaI$.

My researches on polythionates have convinced me that sulphites have the property of desulphurising the tetrathionates, so as to convert them into trithionates. I think, in consequence, that it will be more in accordance with observed facts to admit that the sodium sulphite, which owes its existence to the employment of a reduced quantity of iodine, decomposes the small quantity of sodium tetrathionate produced in the first instance,—



This modified interpretation deprives the interaction of the significance which I had attributed to it in 1874 with reference to the constitution of trithionic acid. I believe, however, that it is nearer to the reality.

The statement ascribed to me by Colefax, although I am not responsible for it, seems, in consequence, to be correct. It is, however, indispensable that the experiments should be performed under exactly the same conditions as those under which I operated when dealing with potassium salts.

13. "The Determination of the Temperature of Steam arising from Boiling Salt Solutions." By J. SAKURAI.

The evidence now on record as to the temperature of the steam arising from boiling salt solutions is exceedingly unsatisfactory. Rudberg has maintained that the temperature of such steam is always the same as that of water boiling under the same pressure, but, under the conditions observed in his experiments, the temperature indicated was evidently not that of the steam, but of a film of liquid water condensed upon his thermometer bulb. Müller came to the conclusion that steam at the moment of its formation within a boiling salt solution has only the temperature of 100°, though it is more or less superheated by rising through the hot solution. Not only is this conclusion difficult to accept on theoretical grounds, but the observations on which it is based are by no means of a convincing character, and are not peculiar to salt solutions.

On the other hand, Faraday and Magnus thought they had proved that the temperature of steam escaping from a boiling salt solution is the same, or nearly the same, as that of the solution, but from the manner in which their experiments were conducted, it is not clear that the temperature they observed was really that of the natural steam escaping from a boiling solution. On the contrary, it would appear that what they determined was essentially the temperature of the wall of the vessel around the thermometer and of the steam superheated thereby.

Such being the case, the author has studied the conditions under which the true temperature of steam escaping from a boiling salt solution may be ascertained, and he has devised a method by which this can be readily effected. The result of his observations is, that the temperature of steam escaping from a boiling salt solution is the same as that of the solution. The most essential conditions for success are:—

1. The thermometer used in ascertaining the temperature of the steam must be kept from contact with the solution—even the smallest drops thrown up by ebullition.

2. The effect of the cooling of the thermometer by radiation must be rendered insignificant in proportion to the heating up by the steam. This condition is readily fulfilled by rapid renewal of the vapour in contact with the thermometer by the expedient of combining the introduction of steam from without with the boiling of the solution by the lamp. Ebullition alone should suffice, but the practical difficulties in the way prevent such being the case; the boiling would have to be tumultuous to generate much vapour, and in a short time the solution would become too concentrated for the experiment to be continued with convenience. On the other hand, by duly regulating the amount of steam entering from without, and the height of the flame, an abundant supply of steam can be secured, and the temperature of the boiling solution may be maintained constant within a few thousandths of a degree for any length of time.

3. The walls of that part of the vessel which serves as the steam chamber for the thermometer must be sufficiently protected from external cooling, and yet, at the same time, must not be heated to the temperature of the steam. Through the non-observance of the former condition as in Rudberg's experiments, so much of the steam is condensed in keeping the walls at 100° that it is hardly possible to keep enough passing over the thermometer bulb, while if the latter condition is ignored, as in Magnus's experiments, the indications of the thermometer may be illusory.

In the apparatus employed this last condition was secured by protecting the steam chamber with a jacket, through which passed a slow stream of the vapour generated by gentle distillation of somewhat dilute acetic acid. By modifying the degree of dilution any desired temperature, changing only slowly as distillation proceeded, was obtained in the jacket; in this manner condensation of steam upon the thermometer bulb, as well as upon the surrounding walls, was prevented.

A salt solution, whose boiling-point had been approximately determined and known to be higher than that of the dilute acetic acid, was boiled, and a rapid current of steam introduced into the boiling solution from without.

The thermometer for ascertaining the temperature of the steam now rose above that in the jacket, and ultimately attained the same temperature as the boiling solution. The following are an example of the results obtained with a solution of calcium chloride.—(See Table).

14. "Note on an Observation by Gerlach of the Boiling Point of a Solution of Glauber's Salt." By J. SAKURAI.

A few years ago G. T. Gerlach (*Zeit. Anal. Chem.*, xxvi., 413) published a paper in which he mentions that steam escaping from a boiling solution of Glauber's salt containing a crystalline magma of the anhydrous salt indicated a temperature of 100°, whilst the liquid is boiling at 82°, or even at 72°. This observation appeared to me so curious and so anomalous that I was induced to repeat his experiments; the results, on the whole, confirmed his observations as to temperatures, but, at the same time, deprived them of all exceptional character. Gerlach describes his experiments in the following words:

"700 grms. of crystallised Glauber's salt were melted in an iron vessel, and kept boiling for some time. The vessel was then removed from the lamp, and the liquid portion of its contents was poured off as completely as possible, whilst the separated anhydrous salt was left in the vessel. The whole was allowed to cool to about 50° before the vessel was again heated. This vessel was now provided with a tin plate cover having two holes, through one of which a thermometer passed, nearly reaching the bottom of the vessel, and through the other a second thermometer, which hung in the steam chamber over the heated crystalline magma.

"The liquid completely boiled at 82° (*Die Flüssigkeit kam schon bei 82° C. vollständig in's Kochen*), whilst the escaping steam showed the temperature of 100°. The temperature of the heated magma rose but very slowly, and only attained a temperature of about 100°, when the mass was almost dry.

"To this almost dry mass I added 100 grms. of crystallised Glauber's salt, which melted on shaking. The crystalline magma now boiled at as low a temperature as 72° C., whilst the steam indicated 100° C." (*Loc. cit.*, 422.)

It is not correct to say that "the liquid completely boils at 82°, whilst the escaping steam has a temperature of 100°," for it is only a wet mass of anhydrous sodium sulphate that is heated. I found that steam in such a case does not uniformly arise from the heated mass, but escapes from a number of channels produced in those portions of it which are in contact with the sides of the vessel, and which are therefore most heated. The central portion of the magma, where the thermometer bulb is placed, is more slowly heated, and hence the fact that while the steam has a temperature of 100°, the wet magma is at a lower temperature.

In the second experiment, in which some crystallised Glauber's salt is added to the heated magma, the temperature of the latter is, for a time, very much lowered, not only because a quantity of a cold substance is introduced, but also because the fusion of the crystallised salt absorbs much heat. The central portions of the mass, therefore, are at as low a temperature as 72° C., whilst the steam which rapidly forms and escapes along the sides of the vessel is at a temperature of 100°. That the latter does not exhibit a higher temperature is easy to understand from the form of the experiment. It is also needless to mention that the temperature of the whole mass soon rises.

Hence Gerlach's observations are erroneous in so far as they imply that a substance can evolve a vapour hotter than itself.

15. "Chemistry of the Thioureas. Part II. (A Preliminary Note)." By EMIL A. WERNER.

In a recent number of the *Berichte* (1892, 48) a paper appeared by A. Bertram entitled "Zur Kenntniss des Monophenylthioharnstoffs und der Imidocarbaminthio-saureester," in which an account is given of the com-

Steam.	Temperature of the		Difference.	
	Solution.	Acetic acid vapour.	(II)–(I).	(I)–(III).
111°2	112°5	110°8	1°3	0°4
111°7	112°5	110°9	0°8	0°8
112°2	112°6	111°1	0°4	1°1
112°5	112°7	111°3	0°2	1°2
112°7	112°9	111°5	0°2	1°2
113°0	113°0	111°6	0°0	1°4
113°1	113°2	111°8	0°1	1°3
113°3	113°3	111°9	0°0	1°4

A meeting of the Committee will be held in June. Fellows desiring grants are requested to make application to the Secretaries before June 15th.

Mr. BLAKESLEY asked if the galvanometer was astatic.

For damping non-astatic ones he had found it useful to wind several turns of wire round the bobbin and put them in series with a few thermoelectric junctions, warmed by the hand, and a key.

In reply, Mr. NALDER said the galvanometer was astatic, but the damping coil could be placed so as to act on one pair of magnets more than on the other.

A paper on "*A Portable Instrument for Measuring Magnetic Fields, with some Observations on the Strength of the Stray Fields of Dynamos*," by E. EDGAR and H. STANSFIELD, was then read.

The instrument was described as an inversion of a d'Arsonval galvanometer, for the torque necessary to maintain a suspended coil conveying a constant current parallel to the field gives a measure of the strength of the field. The constant current is furnished by a Hellensen's dry cell, which the authors found remarkably constant. The instrument consists of a coil of about 50 ohms, wound on mica and suspended by two German silver strips within a tube. A pointer is fixed to the mica and a divided head, to which the outer end of the strip is attached, serves to measure the torsion. Within the head chamber is a commutator which automatically reverses the current in the coil when the head is turned in opposite direction from zero. Two readings may thus be taken to eliminate gravity errors due to want of perfect balance in the coil. Means are provided for adjusting and measuring the tension of the suspensions.

The constant of the instrument was determined by placing the coil in the field of a Helmholtz galvanometer and found to be 0.293 per 1° . Any other field is therefore given by $0.293(n+1)\theta$; where θ is the angle of torsion in degrees, and n the multiple of 50 ohms in series with the coil. Fields from two or three C.G.S. lines upwards can be measured to about 2 per cent by the instrument, and even the earth's field is appreciable.

The authors have tested the fields of dynamos at the Crystal Palace Exhibition and elsewhere, and the results obtained are given in the paper. It is noted that the stray fields of multipolar machines fall off much more rapidly than those of the two-pole dynamos as the distances are increased, and that near edges and corners of the magnets the fields are much stronger than near flat surfaces. The disturbing effect of armature reactions on the strength of the stray fields were measured and shapes of the fields observed in some cases. Experiments on magnetised watches are described in the paper.

Mr. WHIPPLE said the Kew Committee were to some extent responsible for the experiments described, for it was on their account that the investigations were commenced. In connection with the rating of so-called non-magnetic watches, it was necessary to know what strength of fields they were likely to be subjected to. The instrument devised for making the tests was a very interesting one, and he results obtained by it of great value.

Mr. A. P. TROTTER hoped the authors would supplement their work by tracing out the directions of the fields of dynamos, and he described a simple method of doing this by a test needle used as an indiarubber stamp. The question of watches, he thought, must be considered soon; even non-magnetic watches were stopped by being placed in strong fields, owing to Foucault currents generated in the moving parts.

Mr. BLAKESLEY inquired whether the instrument could be used in any position. He thought three observations would be necessary to completely determine any field.

Mr. STANSFIELD, in reply, said they used a pilot needle for showing the direction of the fields and then placed the coil accordingly. The instrument could be used in any position, for the weight of the coil was only about 2 grms. and did not greatly alter the tension of the suspensions, which was usually about 300 grms.

A watch with a brass balance was not influenced by a field of 10 C.G.S. lines, but was seriously affected by one of 40.

Mr. JOSEPH W. LOVIBOND read a paper "*On a Unit of Measurement of Light and Colour*." The paper was illustrated by many coloured charts, diagrams, and models, and several pieces of apparatus by which colour measurements could be made were shown. The principle of the measurements depends on the selective absorption of the constituents of normal white light by coloured glasses (red, yellow, and blue). The depths of tint of the glasses are carefully graduated to give absorptions in numerical proportions. For example, two equal glasses, each called 1-unit red, give the same absorption as a 2-unit red, and so on. The units of red, yellow, and blue are so chosen that a combination of one of each absorb white light without colouring the transmitted light. Such a combination is called a "neutral tint unit." By the use of successive neutral tint units white light can be gradually absorbed without showing traces of colour, and the number of such units required to produce complete absorption is taken as a measure of the intensity or luminosity of the white light.

Methods of representing colours by circles and charts were fully dealt with, and the influence of time of observation on the penetrability of different colours was illustrated by diagrams. The results of 151 experiments on colour mixture were explained and represented diagrammatically.

After the reading of the paper the methods used for colour-matching and measurement were shown by Mr. and Miss LOVIBOND.

Mr. R. W. PAUL exhibited his improved form of Wheatstone bridge arranged to occupy the same space and fulfil the same conditions as the well-known Post Office pattern.

NOTICES OF BOOKS.

Farmyard Manure: its Nature, Composition, and Treatment. By C. M. AIKMAN, B.Sc., F.R.S.E., F.I.C., F.C.S. Edinburgh and London: W. Blackwood and Sons.

THIS treatise, as the author informs us, is essentially a chapter from a work on "*Soils and Manures*," upon which the author is at present engaged. But brief as it is, it contains much valuable matter. Perhaps at first sight it might be imagined that the author was seeking to controvert the views of Ville and others who have insisted on the value of chemical manures: but on careful reading it will be found that such is not Mr. Aikman's intention. He recognises that farmyard manure contains a very small quantity of the three fertilising ingredients, viz., nitrogen, phosphoric acid, and potash; that these three ingredients are present not in the proportion best suited to the requirements of crops, and that two of these ingredients, nitrogen and phosphoric acid, are found not in their most valuable conditions. Hence he considers that the most valuable properties of farmyard manure must be sought for in its indirect influence. He distinguishes the state in which such manure should be applied respectively on different soils. Thus, on heavy clays he recommends the application of manure in a fresh condition, whilst on light soils it should be used when well rotted. He draws a subtle but very rational distinction between manuring the soil and manuring the crop. The former procedure, he holds, cannot in these competitive days be believed in, and he strongly doubts whether farmyard manure is economical as compared with chemical manures. He recognises the truth that urine is not a complete manure and must be supplemented by an addition of phosphates. He admits also that farmyard manure contains too little nitrogen in proportion to its mineral constituents, and that it requires reinforcing firstly with nitrogenous matter, and secondly with phosphates.

We cannot find any decided deliverance on the great question whether it is economical—as it is still commonly

done—to raise cattle for the sake of the manure they produce. Ville, it must be remembered, whilst insisting that the excreta of the stock kept on a farm for labour, for meat, milk, &c., should be fully utilised, contends that to keep cattle for the sake of manure is a capital error. His arguments seem convincing, but it would be desirable to see this subject reconsidered under different conditions. Perhaps Mr. Aikman may see his way to a discussion of this subject in his forthcoming large work. In the meantime, the present treatise must be strongly recommended for the general accuracy of its teachings and the clearness and simplicity of its language. There is here assuredly nothing to bewilder the most purely bucolical mind.

CORRESPONDENCE.

THE PROPOSED CHEMICAL BENEVOLENT FUND FOR NECESSITOUS PROFESSIONAL CHEMISTS OR THEIR WIDOWS AND ORPHANS.

To the Editor of the Chemical News.

SIR,—In 1869 the Council of the Institute of Chemistry proposed to found a Benevolent Fund. The response by the Fellows and Associates was insufficient to warrant further action.

Last year I ventured to suggest that the Jubilee of the Chemical Society be in part celebrated by the foundation of a Benevolent Fund open to the claims of any necessitous chemists or of their widows and orphans. The resulting 184 contributions had a capitalised value of over £5000, and were duly offered to the Society. The Council sympathised with the aims of the Fund, and thanked me for my efforts, but announced that the objects of the Chemical Society were, and must continue to be, restricted to the prosecution of Chemical Science.

I then asked the contributors if the Fund should be organised on a separate and independent foundation. Almost all replied "Yes."

To ascertain whether or not any fair proportion of the members of the four leading Societies of Professional Chemists in practice in the United Kingdom would support the Fund thus commenced, I issued a printed appeal to each of them (3500). The result was most disheartening. The indifference manifested towards the Institute's project was almost as strikingly shown towards this general Chemical Benevolent Fund. My letters had met with abundant response; these circulars produced very little.

I thank the contributors for their kind interest and aid, but clearly we must cease our endeavours to found a Chemical Benevolent Fund, at all events for the present.

The idea of such a Fund is, however, fast growing, and if a few years hence the leaders in the four Societies would unite in urging the matter, I should have no doubt whatever of a permanently successful result. But in any case the majority of the leaders in these Societies must unitedly lead in contributing to the Fund. Then, and then only, will the followers follow. That is the lesson pressed home to me in my much correspondence on this subject.

I have posted to each contributor a printed statement, which includes the substance of this letter, some memoranda relating to organisation which may be useful at a future time, and a complete list of the promised donations and promised annual subscriptions to a separate and independent Chemical Benevolent Fund. The cheques, unasked for, which were sent to me have been returned in full.—I am, &c.,

JOHN ATTFIELD.

Watford, Herts, May 20, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 18, May 2, 1892.

Novel Case of Abnormal Solution. Saturated Solutions.—F. Parmentier.—The author has shown on a former occasion (*Comptes Rendus*, civ., 686) that in the solution of a solid in a liquid it occurs that if the solid is entirely dissolved it is not possible to obtain, as in known cases, a homogeneous mixture by the addition of any quantity whatever of the solvent. A new instance of this fact is the case of bromised ether in ether ($C_4H_{10}OBr_3$). If to this solid substance there is added ether, it dissolves rapidly; but if we add increasing quantities of ether there arrives a moment when the excess of ether separates from the liquid produced. As a definition of saturated solutions comprising the various cases of the solution of solids in the liquids the author adopts the following:—When substances can, without combining, yield a homogeneous liquid, the solution is termed saturated, if one of the substances, added in excess to the solution, separates itself from this solution.

Detection of Fluorine in Varieties of Natural Phosphates.—Ad. Carnot.—The author does not indicate any novel or improved method for the recognition and determination of fluorine in phosphates. For apatites he gives the general formula $Ca(F,Cl)_2 + 3(PO_3CaO)$, in which a little lime may be replaced by an equivalent quantity of magnesia or of ferrous oxide. The semi-crystalline fibrous phosphorites have almost exactly the composition of crystalline apatites. The earthy or compact and slightly concreted phosphorites contain a smaller proportion of fluorine, and those which are very distinctly concreted with a lamellated surface contain only a slight amount of fluorine, which may sometimes almost be neglected. In almost all the sedimentary phosphates the proportion of fluorine is approximately equal to that in apatites containing an equal amount of phosphate. The author purposes studying the transformation undergone by fossil bones.

The Determination of Small Quantities of Carbon Monoxide by Means of Cuprous Chloride.—L. de Saint-Martin.—This memoir cannot be usefully reproduced without the accompanying figure.

Thermic Study of the Function of Phenol.—M. de Forcrand.—This paper does not admit of abstraction.

Determination of the Surface of Ebullition of the Normal Paraffins.—G. Hinrichs.—This paper requires the two accompanying diagrams.

The Action of Pyridic Bases upon Certain Sulphites.—G. Denigès.—The pyridic bases have little disposition to form compounds with the metallic sulphites. The zinc-pyridine and cadmium-pyridine sulphites alone are well defined, and are sufficiently stable to bear washing and drying without dissociation. The zinc-pyridine sulphite is much more stable than the corresponding cadmium salt.

The Preparation and Physical Properties of Acetyl Fluoride.—Maurice Meslans.—The most advantageous method of preparing this compound consists in causing acetyl-chloride to react upon zinc-fluoride previously dried *in vacuo* at 250°. The product thus obtained is a colourless gas which does not fume in the air. It burns with a blue flame, producing a mixture of watery vapour, carbonic acid, and hydrofluoric acid. Its odour resembles that of carbon oxychloride. If inhaled it produces no immediate action, but in a few minutes it occasions oppression, attended with strong bronchial irritation. In larger quantities it may occasion spitting of blood. Water

dissolves about twenty times its own volume, and then decomposes it slowly. Alcohol, ether, benzene, chloroform, &c., dissolve it in every proportion. It is liquefied at the pressure of the atmosphere at 19.5°.

Diamidosulphobenzide and Some of Its Derivatives.—Ch. Lauth.—Diamidosulphobenzide readily yields diazo-derivatives by the action of a nitrite in presence of hydrochloric acid, and these diazo-compounds, on treatment with the usual reagents, yield fine colouring-matters. Scarlets are obtained with α -sulpho- α -naphthol and disulpho- α -naphthol. These colours, contrary to what might have been hoped, have but little affinity for cotton.

Azo- and Alkyl-Compounds of Chrysaniline, and on the Colouring-Substances derived from them.—A. Trillat and De Raczkowski.—The authors' experiments seem to prove that the azo- and alkyl-derivatives of chrysaniline present but a secondary interest from a tinctorial point of view.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 73.

This issue does not contain any chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 8.

This issue contains merely abstracts from other journals.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"The Chemist."—(Reply to J. Cuthbert Welch).—Dr. H. Carrington Bolton's "Catalogue of Scientific Periodicals" (Smithsonian Misc. Coll., vol. xxix.), gives on page 155:—

"The Chemist. . . Edited by Charles Watt and John Watt. 6 vols. 1840-45.

"Continued under the title—

"The Chemist. . . Edited by John Higga Newton. 1 vol. (vii.). 1846-48.

"Continued under the title—

"The Chemist. . . Edited by John and Charles Watt. New Series. 4 vols. 1849-53.

"Continued under the title—

"The Chemist. . . Edited by John and Charles Watt. New Series. 5 vols. 1854-58. ||"

The mark || signifies publication discontinued.—JAS. LEWIS HOWE, Polytechnic Society of Kentucky, Louisville, Ky., April 26, 1892.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. "Recent Bacteriological and Chemical Research in connection with the Fermentation Industries," by Percy F. Frankland, F.R.S. (Cantor Lectures).

TUESDAY, 24th.—Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.

Photographic, 8.

Society of Arts, 8. "The Extension of Colonial Trade," by Colonel Howard Vincent, M.P.

Royal Institution, 3. "Some Aspects of Greek Poetry," by Prof. R. C. Jebb.

WEDNESDAY, 25th.—Society of Arts, 8. "Researches in Photochromy," by F. E. Ives.

Geological, 8.

THURSDAY, 26th.—Royal Institution, 3. "On Faust," by R. G. Moulton, M.A.

Institute of Electrical Engineers, 8.

FRIDAY, 27th.—Royal Institution, 9. "Emotional Expression," by Sir James Crichton-Browne, M.D., F.R.S.

Physical, 5. "On the Present State of Our Knowledge of the Connexion between Ether and Matter—An Historical Summary," by Prof. O. Lodge, F.R.S.

SATURDAY, 28th.—Royal Institution, 3. "Some Modern Discoveries in Agricultural and Forest Botany," by Prof. H. Marshall Ward, F.R.S.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, Burlington House, London, W.

The NEXT ANNUAL GENERAL MEETING will be held at EDINBURGH, commencing on Wednesday, August 3.

President Elect—

SIR ARCHIBALD GEIKIE, LL.D., D.Sc., For. Sec. R.S., F.R.S.E., F.G.S., Director-General of the Geological Survey of the United Kingdom, Corresponding Member of the Institute of France.

NOTICE TO CONTRIBUTORS OF MEMOIRS.—Authors are reminded that the acceptance of memoirs and the days on which they are to be read are, as far as possible, determined by Organising Committees for the several Sections before the beginning of the Meeting. Memoirs should be sent to the office of the Association. Information about local arrangements may be obtained from the Local Secretaries, Edinburgh.

G. GRIFFITH,
Assistant General Secretary.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1696.

COLOURING-MATTER IN SHELL FISH.

By Dr. JAMES LEICESTER,
Merchant Venturers' Technical School, Bristol.

It is a well-known fact that shrimps and lobsters change colour upon boiling, but the exact cause of this, I believe, is still unknown. The following fact may possibly throw some light upon the subject:—

Take a small flask and place about 100 c.c. of concentrated hydrochloric acid in it; then take three or four shrimps, drop them into the acid, cork the flask, and allow to stand for about four hours. The shrimps, of course, must not have been boiled. Very soon a purple colour is noticed close to the tail, from which place, apparently, the majority of the colouring-pigment appears to come.

After about four hours the whole of the liquid is a bright purple colour resembling litmus solution. This colour goes after three or four days, and the solution becomes of a dirty brown colour.

The colouration is not caused by any iodine compound, but is probably of an organic nature. Acetic acid and caustic potash give slightly yellow solutions.

As soon as enough of this pigment can be isolated, one may be able to ascertain if it is the cause of the bright red colour of the fish after boiling.

3, Queen's Parade, Brandon Hill,
Bristol.

ON A

NEW METHOD FOR THE ESTIMATION OF UNSAAPONIFIABLE MATTER IN FATS.

By WILLIAM MANSBRIDGE.

For some years past the ether extraction process has almost universally been employed for the estimation of unsaponifiable matter in fats, and it is now looked upon as the only reliable method.

In spite of its general acceptance, however, it has several drawbacks, of which the most important is, when dealing with some materials, its tediousness. It is often very difficult on this account to obtain concordant results when the analysis is made in duplicate; and even with materials which present least difficulty, sufficient time can seldom be spared if, as in a works' laboratory, several samples have to be examined every day.

The fats most refractory to the ether process are the various qualities of recovered grease and wool-fat, found in commerce under the names of black oil and brown Yorkshire grease.

These bodies contain varying proportions of cholesterin and ischolesterin, together with other alcohols of high molecular weight, of which we have little exact knowledge, and mineral oils from various sources. In addition they may also contain hydrocarbon oils which are not mineral oils, they having been formed in a previous distillation of the oil used for batching the wool. In operating upon such greases, strata intermediate between the soap solution and the ether are formed which effectually prevent the complete separation of the latter; sometimes, indeed, such a perfect emulsion is formed that no separation whatever takes place, rendering it almost impossible to carry the experiment to a satisfactory conclusion.

It being part of my daily work to make a large number

of determinations of unsaponifiable matter, and especially in connection with recovered greases, I soon discovered the imperfections of the ether process; and in the hope of finding something better, I have made a large number of experiments with different solvents, and from the material thus accumulated I worked out the following process. I should state here, however, that since I commenced writing this paper I have been made aware that Hönig and Spitz (*Zeit. für Angew. Chemie*, 1891, 556) in Austria had elaborated and published a process almost identical with this; but as their experiments were almost exclusively carried out on oleines, the present article, dealing with wool-grease and similar bodies, may not be unwelcome as a contribution to the subject.

The solvent which I employ is a fraction of commercial benzoline boiling at 110° F. prepared in the following manner:—Commercial benzoline is distilled in a flask over the water-bath, and the first portion, amounting to about one-fifth of the whole, collected apart; this, when sufficient has been obtained, is re-distilled on the water-bath, in this instance about four-fifths being collected. This should have a boiling-point of 110° F., and should leave no residue on being evaporated; if it fulfil these conditions it may be employed in the analysis. The great advantages of this solvent, which I term "light benzoline," are—its slight solubility in alcohol, permitting a free use of that substance as a washing agent, and its comparatively high boiling-point and consequent slight liability to loss by volatilisation, thus allowing of a higher temperature, which, by rendering the soap solution more fluid, materially assists the separation of the benzoline layer.

In examining a sample I usually take 25 grms. and saponify it in an open basin, or, if considered desirable, under pressure, using alcoholic potash in moderate excess. The soap after boiling with water is decomposed with mineral acid and the fatty acid washed several times with boiling water. By this treatment a mixture of free fatty acids and unsaponifiable matter is obtained. Of this mixture I then take one, two, or four grms., according to the suspected amount of unsaponifiable, arranging the quantity so that about 0.5 gm. is left finally as residue. The portion taken is dissolved in 50 c.c. of methylated spirit, which has previously been saturated with light benzoline, in a conical flask, and 50 c.c. of light benzoline added; the whole is then heated just to boiling under an inverted condenser or a long tube, allowed to cool slightly in order to prevent loss of benzoline, and just neutralised by semi-normal potassic hydrate, the quantity consumed being noted. The contents of the flask are then transferred to a separating funnel, when a very rapid separation of the benzoline carrying the unsaponifiable takes place.

The soapy spirit layer is then removed and 50 c.c. of water at a temperature of 100° F. are added, the whole thoroughly shaken and allowed to stand, when, in cases of a simple admixture of fatty acid and hydrocarbon oil, a very rapid separation takes place; the wash-water is then removed and a further washing with 40 c.c. of warm 70 per cent alcohol is effected. This last completes the removal of traces of soap and also removes water, which, if allowed to remain, would cause objectionable "bumping" in the subsequent distillation. The extraction of the alcoholic soap solution is then repeated and the benzoline washed as before. The two portions may be added and distilled together. Two washings of the alcoholic soap solution have been found sufficient to extract practically all the unsaponifiable matter in any ordinary mixture; crude wool-fat, however, demands a somewhat different treatment. Thus, in dealing with a typical wool-fat, *i.e.*, one containing about 40 per cent cholesterin, &c., I prefer to take 1.0 gm. of the saponified sample, dissolve and neutralise as before, using, however, a rather larger quantity of benzoline. For the first washing I take instead of water the same quantity of 50 per cent alcohol and finish with alcohol as before; four, or even in extreme cases,

five extractions may be necessary, but usually three are sufficient for ordinary accuracy.

As with the ether process, wool-grease of high unsaponifiable content forms intermediate layers of emulsion; but operating as described above I do not find it of sufficient importance to cause much trouble. Should there be, however, any difficulty from this cause, the following manipulation will facilitate the separation:—After shaking up with the first wash-spirit, allow the contents of the separating funnel to rest for about fifteen minutes, then add a few c.c. of nearly boiling alcohol. This so acts on the emulsive layer as to effect an instantaneous liberation of the benzoline; if not quite separated by this treatment more spirit must be added. The wash solutions and spirit should in all cases be reserved for the succeeding extractions, a little of the benzoline being always retained by them, and which, by their being employed over again, is deprived of its unsaponifiable.

The intermediate stratum appears to consist of a slightly soluble soap of a fatty acid having a very high molecular weight. It has recently been examined by J. Lewkowitsch, who found a fatty acid, or mixture of fatty acids, having a high molecular weight.

My own experiments on this subject are confirmatory of those obtained by Dr. Lewkowitsch. This soap forms with the water an emulsion, in which the ascending bubbles of ether, and to a less extent the benzoline, become entangled and effectually retained, sometimes evincing no tendency to separate even after being left for several days.

Many experiments have been made with the view of preventing the difficulty caused by this soapy layer, but, except in the case of warm alcohol, without success. Alcohol appears to act partly by dissolving the soap and partly by reason of its higher temperature, which causes the bubbles to burst and thus set free the benzoline. Used in the way described above I have always found alcohol most effectual.

The distillation may be performed over the water-bath in the usual manner. I prefer, however, to conduct it over the blue flame of an ordinary Argand burner, interposing, if necessary, sufficient wire gauze to modify the heat; it will then usually be found that at the end of the distillation sufficient heat remains in the flask to finish the driving off of the benzoline, which may safely be accomplished by blowing into the warm flask while it is slowly rotated. It is very desirable that the final "drying" should be performed as expeditiously as possible, otherwise large quantities of the unsaponifiable matter may be driven off with the benzoline. Of course, if the unsaponifiable should be very volatile, the distillation must be conducted over the water-bath; suitable precautions should also be observed in the preliminary saponifications.

I have found the method of "drying" over the argand to give results much more accurate than are usually obtained by heating on the water-bath. It is well known that mineral oils, even those of high specific gravity and boiling-point, lose a considerable proportion of their weight if they are retained at comparatively low temperatures for long periods of time, and if they are exposed in thin films the loss is relatively very great; thus if the small amount of ether extract, which in the majority of cases consists entirely of mineral oil, is kept at the temperature of the water-bath for an hour it may lose sufficient to make a difference of 2 to 3 per cent in the calculation of the results.

This objection does not apply to the use of the Argand burner as described above, as is shown by the following experiments:—About 0.5 gm. of pure mineral oil of various specific gravities was introduced to the distillation flask, benzoline was added in the same quantity as was used for the extraction, and the distillation conducted precisely as described for actual analysis; the residue was weighed, and the flask transferred to the water-bath, and

again weighed at intervals of $\frac{1}{2}$, $1\frac{1}{2}$, and 3 hours, with the following results:—

I.—Scotch Mineral Oil (Specific Gravity 0.885).

Quantity taken	0.612 grm.
1st weighing after distillation on Argand ..	0.612 "
After $\frac{1}{2}$ hour on water-bath	0.597 "
After $1\frac{1}{2}$ hours on water-bath	0.585 "
" 3 " " " " " " " " " " " "	0.584 "

Loss after 3 hours' heating on water-bath = 4.248 p.c.

II.—American Mineral Oil (Specific Gravity 0.896).

Quantity taken	0.620
After distillation and weighing on Argand ..	0.619
After $\frac{1}{2}$ hour on water-bath	0.614
After $1\frac{1}{2}$ hours on water-bath	0.609
" 3 " " " " " " " " " " " "	0.603

Loss after 3 hours' heating on water-bath = 2.743 p.c.

The process has been employed constantly for the last nine months in the laboratory, where the author is engaged, always with satisfactory results. The residues have occasionally been examined for soap, but only on rare occasions has any been detected, and then only in slight traces.

The accompanying results are adduced as showing the accuracy attainable; they are representative, not having been in any way selected.

1. *Pure Wool-Fat*.—These samples were typical Yorkshire brown greases, containing about 25 per cent of free fatty acids; the remainder, with the exception of 2 or 3 per cent, being cholesterin ethers of stearic, palmitic, and oleic acids. They were treated exactly as above described for wool-fat; an intermediate stratum was formed but did not render any difficulty.

	Unsap. by Extraction.	By Titration.
(i.) Wool-fat	29.05 per cent	39.36
Duplicate	29.25 "	—

	Unsap. by Extraction.	By Titration.
(ii.) Wool-fat	41.70	46.79
Duplicate	41.70	—

2. *West of England Recovered Grease*.—This is a grease recovered from wool-washing, which contains about 60 per cent free fatty acids, the remainder being cholesterin ethers; it may be classed as a semi-wool-fat. It presents the same difficulties to the extraction as the pure wool-fat.

	Unsap. by Extraction.	By Titration.
(i.) West of England grease	21.55	23.16
Duplicate	21.05	23.16

	Unsap. by Extraction.	By Titration.
(ii.)	22.81	23.63

3. *Distilled Wool-Fat*.—No. 1, (ii.), after distillation with superheated steam. By distillation a large proportion of the cholesterin and similar bodies is broken up into hydrocarbon oils, which by their presence cause an easier and more complete separation of the benzoline; the intermediate stratum in this case was very slight.

	By Extraction.	By Titration.
(i.) Distilled wool-fat, No. 1, (ii.)	52.25	48.64
Duplicate	51.90	48.64

4. *Oleine from Distilled Wool-Fat*.—This is the fluid portion of the fatty acids separated by pressure from the solid acids (stearine).

	Unsap. by Extraction.	By Titration.
(i.)	44.35	44.31
Duplicate	44.25	—
(ii.)	50.25	47.13
Duplicate	50.35	—

The benzoline layer from these analyses and from No. 3, was washed with water, no intermediate layer was formed, and quick and perfect separation took place.

5. *Black Recovered Grease.*—These are greases of low quality which have been scoured from shoddy, &c. They contain about 5 per cent of cholesterin ethers, usually a large quantity of mineral oils varying from 20 to 45 per cent, the remainder being free fatty acids; they do not form such obstinate intermediate strata as wool-fat, and may be examined as described in the first section of the process. The benzoline layer often separates rapidly and completely, and their analysis is easily accomplished.

	Unsap. by Extraction.	By Titration.
Black recovered grease ..	22'61	25'55
Duplicate	22'72	—

It will be seen from the above results that except in the case of pure wool-fat there is a tolerably close agreement between the results obtained by this process and those arrived at by titration (expressed in terms of oleic acid, 282), thus indicating that for practical purposes simple titration, even with unknown greases of low quality, is a near approximation to the real contents of unsaponifiable matter; the difference is certainly not greater than is usually found between the reports of different analysts when the ether process is employed. In the case of pure wool-fats my experience has shown that there is a tolerably constant relation between the results obtained by extraction with benzoline and the titration values, such relation depending on the amount of cholesterin and similar bodies in the grease. The connection is sufficiently constant to allow of its use for determining the presence of mineral oil or resin oil in wool-fat, and thus give a valuable indication as to the purity or otherwise of the sample.

RESEARCHES ON THE METALS OF THE CERIUM GROUP.*

TREATISE I.

By P. SCHÖTTLANDER.

(Concluded from p. 244).

THE crystallisation is continued as far as the eighth series, the last (usually small) portions of the mother-liquor of each series and the last mother-liquor of the ninth series being added to the ultimate fraction, and thus everything non-crystallisable is removed from the main material. Hereupon the fractions of Series 8 were united with the above-mentioned fractions of didymium, which had been set aside, and the crystallisation was continued as far as Series 14.

Here it appeared that by no means only those constituents of didymium to which Auer von Welsbach has given the name praseodymium pass over into the first lanthaniferous fractions, but at the same time also very noticeable quantities of those which form the more readily soluble double ammonium nitrates. In order, therefore, to carry the separation as far as possible, it is not sufficient to remove all the lanthanum from the first green didymium fractions, but a very large number of crystallisations must be carried on in order to transport these more readily soluble constituents to the corresponding fractions at the end of the series.

The bulk of the green lanthanum salts obtained was separately further fractionated for complete purification, and yielded finally two main fractions, La fraction I. containing 119 grms. lanthanum oxide, and La fraction II. with 152 grms. These two fractions, almost saturated solutions of the ammonium double nitrates, when examined with the spectroscope showed no trace of absorption

bands in strata of 12 to 15 c.m. in thickness, but nevertheless contained traces of praseodymium, since the lanthanum oxide obtained from both had a slight reddish cast, and as the La fraction I. was almost entirely, and the La fraction II. in part, submitted again to a fractionated crystallisation of the ammonium double salts, and the last mother-liquors were concentrated down to 1 or 2 c.c. and again examined with the spectroscope, faint indications of the three praseodymium bands were recognised in the blue and the violet.

Upon these two fractions there followed six smaller fractions, in which the green colouration appeared constantly stronger and more distinct.

Of the didymium fractions the earliest green ones, up to the twenty-first and twenty-second series, and the following intermediate fractions were further fractionated even up to the twenty-fifth series; with the mean and last fractions the process was continued only to the fifteenth and sixteenth series.

In order to effect the completest possible separation of the crystallisable and the non-crystallisable constituents, the last mother-liquors from the tenth series were not taken directly to the final fraction, but were first collected into two transition fractions. Of these the first was re-crystallised twice, the two last mother-liquors were added to the second fraction; the second fraction was then similarly twice re-crystallised, and the two resulting mother-liquors were united to the final fraction. The pure crystals of the first transition fraction, corresponding to about 12 grms. of oxide, and those of the second representing about 20 grms. of oxide, were preserved separately.

After nearly 3000 crystallisations had been carried out (including the crystallisations of the lanthanum fractions), the entire residual didymium material yielded twenty-three fractions, in which lanthanum could be supposed as present only in the three first. The absorption spectra of these twenty-three fractions and of the final fraction will be fully discussed in the second treatise.

THE SOLUBILITY OF VARIOUS INORGANIC SALTS IN ACETONE AND OF ACETONE IN DEXTROSE SOLUTIONS.*

By W. H. KRUG and K. P. McELROY.

WE have investigated the solubility of some inorganic salts in acetone, the results being embodied in the following tables:—

Chlorides.

Sodium chloride.. ..	Insoluble.
Potassium chloride	"
Ammonium chloride	"
Calcium chloride	Very sparingly soluble.
Barium chloride	"
Strontium chloride (anhydrous)	"
Ferric chloride	Freely soluble.
Zinc chloride (in sticks)	"
Cobaltous chloride (anhydrous)	"
Nickelous chloride (anhydrous)	Insoluble.
Cadmium chloride (anhydrous)	Somewhat soluble.
Mercuric chloride	Very freely soluble.
Mercurous chlorides	Insoluble.

Bromides.

Potassium bromide	Slightly soluble.
Sodium bromide	"
Cadmium bromide (anhydrous)	Freely soluble.

Iodides.

Potassium iodide.. ..	Soluble.
Mercuric iodide	"

* *Berichte der Deutsch. Chem. Gesell.*

* Read before the Washington Chemical Society, March 10, 1892. From the *Journal of Analytical and Applied Chemistry*, vi., No. 4.

Cyanides and Sulphocyanides.

Mercuric cyanide	Freely soluble.
Potassium sulphocyanide	" "
Ammonium sulphocyanide	" "
Ferric sulphocyanide	Soluble.
Cobaltous sulphocyanide	" "
Nickelous sulphocyanide	Insoluble.

Nitrate and Nitrites.

Sodium nitrate	Very slightly soluble.
Potassium nitrate	" "
Ammonium nitrate	Slightly soluble.
Barium nitrate	Insoluble.
Bismuth nitrate	" "
Lead nitrate	Very slightly soluble.
Silver nitrate	Soluble.
Potassium nitrate	Very slightly soluble.

Carbonates.

Potassium carbonate	Insoluble.
Sodium carbonate (anhydrous) ..	" "

Sulphates and Sulphites.

Copper sulphate (anhydrous) ..	Insoluble.
Potassium sulphate	" "
Ferric sulphate (anhydrous) ..	" "
Ferrous ammonium sulphate (crystalline)	" "
Ferrous sulphate (anhydrous) ..	" "
Calcium sulphite	" "

Acetates.

Zinc acetate (crystalline)	Soluble.
Copper acetate (crystalline) ..	Slightly soluble.
Lead acetate (crystalline)	" "
Magnesium acetate	Insoluble.
Sodium acetate	" "
Calcium acetate	" "

Miscellaneous.

Potassium ferricyanide	Insoluble.
Boric acid	Freely soluble.
Mercuric sulphide	Insoluble.
Potassium chlorate	Very slightly soluble.
Ferric pyrophosphate	Insoluble.
Ammonium molybdate	" "
Ammonium oxalate	" "
Ammonium tartrate	" "
Cupric chloride (crystalline) ..	Freely soluble.
Nickelous sulphate (crystalline) ..	Very sparingly soluble.
Lithium chloride (crystalline) ..	Soluble.
Cobaltous nitrate (crystalline) ..	Freely soluble.
Nickelous nitrate (crystalline) ..	Sparingly soluble.
Malic acid	Freely soluble.
Tartaric acid	" "
Oxalic acid	" "

The solubility at 25° C. has been determined quantitatively for the following :—

Substance.	100 parts acetone by weight dissolve—
Potassium iodide	2.930
Potassium bromide	0.023
Mercuric chloride	50.990
Mercuric iodide	2.090
Cobaltous chloride (anhydrous) ..	8.620

The behaviour of acetone with dextrose solutions is similar to that with sugar solutions. The solubility of acetone in dextrose solutions, ranging from 10 to 50 per cent, was determined for 25° C. The method used was the same as that applied to determine the solubility of acetone in sugar solutions.

100 Grms. Dextrose Solutions Dissolve at 25° C.

Per cent dextrose.	Grms. acetone.
10.. ..	747.86
20.. ..	237.71
30.. ..	146.30
40.. ..	72.72
50.. ..	32.70

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, May 12th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, the whole were found to be clear, bright, and well filtered.

The satisfactory condition of the water supply to the Metropolis exhibited throughout the preceding months of the year has been more than maintained during the past month. But in respect to the results indicative of the nearly always minute proportion of organic matter present in the water, so long as the figures continue low, too much stress must not be laid on their monthly or even weekly variations. According to the more or less favourable meteorological conditions affecting the river from time to time, these figures will vary more or less, and have, during the past month, proved to be exceptionally low.

Thus, taking the Thames-derived water for comparison—and a similar result is apparent in the case of the New River and East London Companies' supplies—the mean amount of organic carbon present in the April supply was only 0.125 part in 100,000 parts of the water, as against a mean for the January supply of 0.158 part, and a mean for the first three months of the year of 0.146 part in 100,000 parts of the water.

But even as between the January and April supplies, the difference in the mean proportions of organic carbon present, or 0.033 part in 100,000 parts, is quite immaterial, corresponding as it does to about the one-seventeenth part of a grain of organic matter in a gallon (i.e., 70,000 grains) of the water.

A comparison, in the case of the Thames-derived supplies, of the results obtained during the past month, and the mean results afforded by the previous three months, is given below, but the notably low figures furnished by the past month's supply one can scarcely expect to be continuously maintained :—

	Ratio of brown to blue tint. Means.	Oxygen re- quired for oxidation. Means.	Organic carbon per 100,000. Means.	Organic carbon per 100,000. Maxima.
First three months	9'8 : 20	0'045	0'146	0'204
April ..	5'6 : 20	0'033	0'125	0'147

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

AN ALLEGED NEW ELEMENT.

THE *Chemiker Zeitung* gives the following particulars concerning masrium, a supposed new element obtained from an Egyptian mineral:—This mineral, found by Johnson Pasha in 1890, was known at first as Johnsonite, but has since been re-named masrite. Richmond and Off found in this mineral cobalt, which attracted attention, as no Egyptian ore of this metal was yet known. A large sample of the mineral (150 kilos.) was conveyed to the Government Laboratory, and was found to contain—

Water	40'39
Alumina	10'62
Ferric oxide	1'63
Masrium oxide	0'20
Manganous oxide	2'56
Cobalt oxide	1'02
Ferrous oxide	4'23
Sulphuric acid	36'78

The mineral was dissolved in water and precipitated with hydrogen sulphide in an acetic solution. In place of the black cobalt sulphide there fell at first a white precipitate, which was allowed to subside. From it, after a somewhat circumstantial treatment, an approximately pure hydroxide was obtained. The atomic weight of masrium was determined as 228. It forms only one oxide, MsO , a white substance. The sulphate, $\text{MsSO}_4 \cdot 8\text{H}_2\text{O}$, is a white salt, which crystallises badly from water, but readily from a 50 per cent alcohol. It forms an alum and a double salt with potassium sulphate.

The reactions of masrium are:—Hydrochloric acid produces no precipitation; sulphuretted hydrogen gives no precipitate in presence of hydrochloric acid, but a white precipitate in presence of acetic acid. Ammonia throws down white masrium hydroxide insoluble in excess. Ammonium sulphide and ammonium carbonate give white gelatinous precipitates insoluble in excess of the precipitant and in ammonia. Ammonium phosphate gives a white precipitate insoluble in excess of phosphate and in ammonia. Caustic alkalis give a white precipitate soluble in excess. Potassium ferrocyanide gives a white precipitate insoluble in excess of ferrocyanide and in dilute hydrochloric acid, but soluble in excess of masrium chloride. Ferricyanide gives no precipitate. Ammonium acetate give a precipitate in a boiling solution of masrium, which re-dissolves on cooling. Potassium chromate gives a yellow precipitate soluble in excess of masrium chloride. Potassium tartrate gives a white precipitate soluble in excess. The free metal has not been obtained, neither has any vapour density been determined nor spectroscopic examination effected.

(There is evidently here need for verification and further investigation).

Constitution of the Carbide Derivative of Perseite.
—L. Maquenne.—The xylene hydrides, C_8H_{16} , derived from camphoric acid yield with bromine and aluminium chloride the same reaction as toluene hexahydride. It is the same with the naphthenes.—*Comptes Rendus*, cxiv., No. 9.

METHODS FOR THE DETERMINATION OF NITROGEN.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

THE ABSOLUTE OR CUPRIC OXIDE METHOD.

(Applicable to all nitrogen determinations).

The apparatus and reagents needed are as follows:—

Apparatus.

Combustion tube of best hard Bohemian glass, about 26 inches long and $\frac{1}{2}$ inch internal diameter.

Azotometer of at least 100 c.c. capacity, accurately calibrated.

Sprengel mercury air-pump.

Small paper scoop, easily made from stiff writing-paper.

Reagents.

Cupric Oxide (coarse).—Wire form; to be ignited and cooled before using.

Fine Cupric Oxide.—Prepared by pounding ordinary cupric oxide in mortar.

Metallic Copper.—Granulated copper or fine copper gauze reduced and cooled in stream of hydrogen.

Sodium Bicarbonate.—Free from organic matter.

Caustic Potash Solution.—Dissolve commercial stick potash in less than its weight of water so that crystals are deposited on cooling. When absorption of carbonic acid ceases to be prompt, solution must be discarded.

Loading Tube.

Of ordinary commercial fertilisers take 1—2 grms. for analysis. In the case of highly nitrogenous substances the amount to be taken must be regulated by the amount of nitrogen estimated to be present. Fill tube as follows: (1) about 2 inches of coarse cupric oxide. (2) Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analysed, about 4 inches of the tube; pour on this the substance, rinsing watch-glass with a little of the fine oxide, and mix thoroughly with spatula; pour into tube, rinsing the scoop with a little fine oxide. (3) About 12 inches of coarse cupric oxide. (4) About 3 inches of metallic copper. (5) About 2½ inches of coarse cupric oxide (anterior layer). (6) Small plug of asbestos. (7) Eight-tenths to 1 gm. of sodium bicarbonate. (8) Large loose plug of asbestos; place tube in furnace, leaving about 1 inch of it projecting; connect with pump by rubber stopper smeared with glycerin, taking care to make connection perfectly tight.

Operation.

Exhaust air from tube by means of pump. When a vacuum has been obtained allow flow of mercury to continue, light gas under that part of the tube containing metallic copper, anterior layer of cupric oxide (see 5th above) and bicarbonate of soda. As soon as vacuum is destroyed, and apparatus filled with carbonic acid gas, shut off the flow of mercury, and at once introduce the delivery tube of the pump into the receiving arm of the azotometer, and just below the surface of the mercury seal of the azotometer, so that the escaping bubbles will pass into the air and not into the azotometer, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm so that the bubbles will escape into the azotometer. Light the jets under the 12-inch layer of oxide, heat gently for a few moments to drive out any moisture that may be present, and bring to red heat. Heat gradually mixture of substance and oxide, lighting one jet at a time. Avoid too rapid evolution of bubbles, which should be allowed to escape at rate of about one per second or a little faster.

When the jets under mixture have all been turned on light jets under layer of oxide at end of tube. When evolution of gas has ceased, turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with pump and remove azotometer before flow of mercury is stopped. Break connection of tube with pump, stop flow of mercury, and extinguish lights. Allow azotometer to stand for at least an hour, or cool with stream of water until permanent volume and temperature are reached.

Adjust accurately the level of the KOH solution in bulb to that in azotometer, note volume of gas, temperature, and height of barometer; make calculations as usual. The labour of calculation may be much diminished by the use of the tables prepared by Messrs. Battle and Dancy, of the North Carolina Experiment Station (Raleigh, N.C.).

The above details are, with some modifications, those given in the report of the Connecticut Station for 1879 (p. 124), which may be consulted for details of apparatus, should such details be desired.

THE KJELDAHL METHOD.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

1. Standard hydrochloric acid whose absolute strength has been determined:—(a) By precipitating with silver nitrate and weighing the silver chloride as described in Crookes's "Select Methods," p. 571; (b) by potassium tetra-oxalate which has been purified by re-crystallising two or three times; (c) by determining the amount neutralised by the distillate from a weighed quantity of pure ammonium chloride boiled with an excess of sodium hydrate. Half normal acid, *i.e.*, containing 18.23 grms. hydrochloric acid to the litre, is recommended. Cochineal or dimethyl-aniline orange to be used as the indicator in standardising the acid.

2. Standard ammonia, whose strength, relative to the acid, has been accurately determined. One-tenth normal ammonia, *i.e.*, containing 0.7 gm. ammonia to the litre, is recommended for accurate work.

3. "C. P." sulphuric acid, specific gravity 1.83, free from nitrates and also from ammonia sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen. Eimer and Amend's "Strictly C. P." is good.

4. Metallic mercury or mercuric oxide, HgO, prepared in the wet way. That prepared from mercury nitrate cannot safely be used.

5. Potassium permanganate tolerably finely pulverised.

6. Granulated zinc, pumice stone, or one-half gm. of zinc dust to be added to the contents of the flasks in distillation, when found necessary in order to keep from bumping.

7. A solution of 40 grms. of commercial potassium sulphide in 1 litre of water.

8. A saturated solution of sodium hydrate free from nitrates, which are sometimes added in the process of manufacture to destroy organic matter and improve the colour of the product. That of the Greenbank Alkali Company is of good quality.

9. Solution of cochineal prepared according to Fresenius's "Quantitative Analysis," second American edition, p. 679.

10. Kjeldahl's digestion flasks of hard, moderately thick, well-annealed glass. These flasks are about nine inches long, with a round, pear-shaped bottom, having a maximum diameter of 2½ inches, and tapering out gradually in a long neck, which is three-fourths of an inch in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225–250 c.c.

11. Distillation flasks of ordinary shape, of 550 c.c. capacity, or preferably flasks of the same capacity, of pear-shaped bottom, of well-annealed glass, for both digestion and distillation, and fitted with a rubber stopper

and a bulb tube above to prevent the possibility of sodium hydrate being carried over mechanically during distillation. The bulbs are about 1½ inches in diameter, the tubes being the same diameter as the condenser, and cut off obliquely at the lower end. This is adjusted to the tube of the condenser by a rubber tube.

12. A Condenser.—Several forms have been described, no one of which is equally convenient for all laboratories. The essential thing is that the tube which carries the steam to be condensed shall be of block-tin. The upper ends of the tin tubes should be bent so that the glass connections may have a slope toward the distilling flasks. All kinds of glass are decomposed by steam and ammonia vapour, and will give up alkali enough to impair accuracy. (See Kreussler and Henzold, *Ber. Berichte*, xvii., p. 34). The condenser in use in the laboratory of the Connecticut Experiment Station, devised by Prof. Johnson, consists of a copper tank, supported by a wooden frame, so that its bottom is 11 inches above the work-bench on which it stands. This tank is 16 inches high, 32 inches long, and 3 inches wide from front to back, widening above to 6 inches. It is provided with a water-supply tube which goes to the bottom, and a larger overflow pipe above. The block-tin condensing tubes, whose external diameter is three-eighths of an inch, seven in number, enter the tank through holes in the front side of it near the top, above the level of the overflow, and pass down perpendicularly through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 1½ inches below the bottom of the tank, and are connected by short rubber tubes with glass bulb tubes of the usual shape, which dip into precipitating beakers or Erlenmeyer flasks of about 300 c.c. capacity. The titration can be made directly in them. The distillation flasks are supported on a sheet-iron shelf, attached to the wooden frame that supports the tanks in front of the latter. Where each flask is to stand a circular hole is cut, with three projecting lips, which support the wire gauze or asbestos under the flask, and three other lips, which hold the flask in place and prevent its moving laterally out of place while distillation is going on. Below this sheet-iron shelf is a metal tube carrying seven Bunsen burners, each with a stop-cock like those of a gas-combustion furnace. These burners are of a larger diameter at the top, which prevents smoking when covered with fine gauze to prevent the flame from striking back.

13. The stand for holding the digestion flasks consists of a pan of sheet-iron 29 inches long by 8 inches wide, on the front of which is fastened a shelf of sheet-iron as long as the pan, 5 inches wide and 4 inches high. In this are cut six holes 1½ inches in diameter. At the back of the pan is a stout wire running lengthwise of the stand, 8 inches high, with a bend or depression opposite each hole in the shelf. The digestion flask rests with its lower part over a hole in the shelf and its neck in one of the depressions in the wire frame, which holds it securely in position. Heat is supplied by low Bunsen burners below the shelf. With a little care the naked flame can be applied directly to the flask without danger.

The Determination.

1. The Digestion.—Seven-tenths to 2.8 grms. of the substance to be analysed, according to its proportion of nitrogen, is brought into a digestion flask with approximately 0.7 gm. of mercuric oxide, or its equivalent in metallic mercury, and 20 c.c. of sulphuric acid. The flask is placed on the frame above described, in an inclined position, and heated below the boiling-point of the acid for from five to fifteen minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be added to prevent it. The heat is then raised until the acid boils briskly. No further attention is required till the contents of the flask have become a clear liquid, which is colourless, or at least has only a very pale straw colour. The flask is then removed from the frame, held upright, and while still hot, potassium

permanganate is dropped in carefully and in small quantity at a time till, after shaking, the liquid remains of a green or purple colour.

2. *The Distillation.*—After cooling, the contents of the flask are transferred to the distilling flask with about 200 c.c. of water, and to this a few pieces of granulated zinc, pumice stone, or one-half grm. of zinc dust when found necessary to keep the contents of the flask from bumping, and 25 c.c. of potassium sulphide solution are added, shaking the flask to mix its contents. Next add 50 c.c. of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 c.c. of the distillate will generally contain all of the ammonia. This operation usually requires from forty minutes to one hour and a half. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in cases of substance most difficult to oxidise, and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. Potassium sulphide removes all mercury from solution, and so prevents the formation of mercurio-ammonium compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen, and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present which might otherwise escape notice.

*Kjeldahl Method Modified to Include the Nitrogen of Nitrates.**

(Applicable to all fertilisers containing nitrates).

Besides the reagents and apparatus given under the Kjeldahl method there will be needed—

1. Zinc dust. This should be an impalpable powder; granulated zinc or zinc filings will not answer.
2. Zinc sulphide.
3. Commercial salicylic acid.

The Determination.

Bring from 0.7 to 1.4 grm. of the substance to be analysed into a Kjeldahl digesting flask, add to this 30 c.c. of sulphuric acid containing 2 grms. of salicylic acid, and shake thoroughly; then add *gradually* 2 grms. of zinc dust, shaking the contents of the flask at the same time, or add to substance 30 c.c. of sulphuric acid containing 1 grm. of salicylic acid; then add direct 2 grms. of zinc sulphide. Finally, place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly, and the boiling continued until white fumes no longer pour out of the flask. This requires about five or ten minutes. Add now approximately 0.7 grm. mercuric oxide, or its equivalent in metallic mercury, and continue the boiling until the liquid in the flask is colourless, or nearly so. (In case the contents of the flask are likely to become solid before this point is reached, add 10 c.c. more of sulphuric acid). Complete the oxidation with a little permanganate of potash in the usual way, and proceed with the distillation as described in the Kjeldahl method. The reagents should be tested by blank experiments.

THE RUFFLE METHOD.

Apparatus and Reagents.

1. Standard solutions and indicator the same as for the Kjeldahl method.

2. A mixture of equal parts by weight of fine slaked lime and finely powdered crystallised sodium hyposulphite.

3. A mixture of equal parts by weight of finely powdered granulated sugar and flowers of sulphur.

4. Granulated soda-lime, as described under the soda-lime method.

5. Combustion tubes of hard Bohemian glass, 20 inches long and $\frac{1}{4}$ inch in diameter.

6. Bulbed U-tubes or Will's bulbs, as described under the soda-lime method.

Preparation.

1. Clean, and fill the U-tube with 10 c.c. of standard acid.

2. Fit cork and glass connecting tube. Fill the tube as follows:—(1). A loosely fitting plug of asbestos, previously ignited, and then 1 to 1 $\frac{1}{2}$ inches of the hyposulphite mixture. (2). The weighed portion of the substance to be analysed is intimately mixed with from 5 to 10 grms. of the sugar and sulphur mixture. (3). Pour on a piece of glazed paper, or porcelain mortar, a sufficient quantity of the hyposulphite mixture to fill about 10 inches of the tube; then add the substance to be analysed, as previously prepared; mix carefully and pour into the tube; shake down the contents of the tube; rinse off the paper or mortar with a small quantity of the hyposulphite mixture and pour into the tube; then fill up with soda lime to within 2 inches of the end of the tube. (4). Place another plug of ignited asbestos at the end of the tube and close with a cork. (5). Hold the tube in a horizontal position, and tap on the table until there is a gas channel all along the top of the tube. Make connection with the U-tube containing the acid, aspirate, and see that the apparatus is tight.

The Combustion.—Place the prepared combustion tube in the furnace, letting the open end project a little so as not to burn the cork. Commence by heating the soda lime portion until it is brought to full red heat. Then turn on slowly jet after jet toward the outer end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U-tube begins to recede toward the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube and wash the contents into a beaker or porcelain basin, add a few drops of the cochineal solution, and titrate.

THE SODA LIME METHOD.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

1. Standard solutions and indicator the same as for the Kjeldahl method.

2. Granulated soda lime, fine enough to pass a 10-mesh sieve, and thoroughly dry.

3. Fine soda lime, fine enough to pass a 20-mesh sieve, also thoroughly dry.

To prepare soda lime of the required fineness, the coarse granulated article of the trade may be ground until it will pass through a sieve of about ten-hundredths inch mesh. It is then sifted on a sieve of about twenty-hundredths inch mesh to separate the fine from the coarse. The two portions are then thoroughly dried in the air bath, or by heating in a porcelain dish or iron pan over a lamp, stirring constantly.

Excellent soda lime may be easily and cheaply prepared according to the directions of Professor Atwater (*Am. Chem. Journal*, ix., p. 312), by slaking 2 $\frac{1}{2}$ parts of quicklime with a strong solution of 1 part commercial caustic soda (such soda as is used in the Kjeldahl process), care being taken that there is enough water in the solution to

* Described by Prof. M. A. Scovell.

slake the lime. The mixture is then dried and heated in an iron pot to incipient fusion, and when cold ground and sifted as above.

Instead of soda lime, Johnson's mixture of carbonate of soda and lime or slaked lime may be used.

Slaked lime may be granulated by mixing it with a little water to form a thick mass, which is dried in the water oven until hard and brittle. It is then ground and sifted as above. Slaked lime is much easier to work with than soda lime, and gives excellent results, though it is probable that more of it should be used in proportion to the substance to be analysed than is the case with soda lime.

4. Asbestos which has been ignited and kept in a glass stoppered bottle.

5. Combustion tubes about 40 c.m. long, and about 12 m.m. internal diameter; drawn out to a point and closed at one end.

6. Large bulbed U-tubes with glass stopcock or Will's tubes with four bulbs.

The Determination.

The substance to be analysed should be powdered fine enough to pass through a sieve of 1 m.m. mesh; 0.7 to 1.4 grms., according to the amount of nitrogen present, is taken for the determination. Into the closed end of the combustion tube put a small loose plug of asbestos, and upon it about 4 c.m. of fine soda lime. In a porcelain dish or mortar mix the substance to be analysed thoroughly, but quickly, with enough fine soda lime to fill about 16 c.m. of the tube, or about 40 times as much soda lime as substance, and put the mixture into the combustion tube as quickly as possible by means of a wide-necked funnel, rinsing out the dish and funnel with a little more fine soda lime, which is to be put in on top of the mixture. Fill the rest of the tube to about 5 c.m. of the end with a granulated lime, making it as compact as possible by tapping the tube gently while held in a nearly upright position during the filling. The layer of granulated soda lime should be not less than 12 c.m. long. Lastly, put in a plug of asbestos about 2 c.m. long, pressed rather tightly, and wipe out the end of the tube to free it from adhering soda lime.

Connect the tube by means of a well-fitting rubber stopper or cork, with the U-tube or Will's bulbs containing 10 c.c. standard acid, and adjust it in the combustion furnace so that the end projects about 4 c.m. from the furnace, supporting the U-tube or Will's bulb suitably. Heat the portion of the tube containing the granulated soda lime to moderate redness, and when this is attained extend the heat gradually through the portion containing the substance so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of the first part until the whole tube is heated uniformly to the same degree. Keep up the heat until gases have ceased bubbling through the acid in the bulbs and the mixture of substance and soda lime has become white or nearly so, which shows that the combustion is finished. The combustion should occupy about three-quarters of an hour, or not more than one hour. Remove the heat, and when the tube has cooled below redness break off the closed tip and aspirate air slowly through the apparatus for two or three minutes to bring all the ammonia into the acid. Disconnect, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion the end of the tube projecting from the furnace must be kept heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion tube.

It is found very advantageous to attach a Bunsen valve to the exit tube, allowing the evolved gases to pass out freely, but preventing a violent "sucking back" in case of a sudden condensation of steam in the bulbs.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 245).

SINCE the silica and alumina are probably present as sodic silicate and aluminate in the original carbonate, and may be considered as replacing carbon dioxide molecule for molecule, it is evident that the correction to be applied will not equal the whole weight of the residue. Upon this assumption the correction when phenolphthalein is used as an indicator amounts to about half the weight of the impurity, or about 0.007 per cent of the weight of the sodic carbonate. Toward methyl orange aluminic hydroxide is alkaline; hence in this case the errors due to the two impurities tend to counterbalance each other, and the correction may be omitted. The presence of a small amount of alumina thus explains the slight difference observed later between the results obtained with these two indicators.

The crystallised sodic carbonate was dried over pure boiled sulphuric acid in a vacuum, and subsequently ignited to a dull red heat in a double crucible over a Berzelius spirit lamp. The latter apparatus was employed in order to avoid the possible introduction of impurity from illuminating gas. It was found that the salt could be ignited to perfectly constant weight at any temperature between dull redness and its fusing point. The light powder contracts and "sinters together" at a low red heat, and then remains essentially unchanged in weight until it melts. The unfused salt was not observed to gain perceptibly in weight upon an hour's exposure to the air of the balance case; upon the other hand, the fused salt, which of course was never used as a basis of determination, was markedly hygroscopic.

Acids.—The chemically pure hydrochloric and nitric acids were each distilled three times successively in a platinum still. Large quantities evaporated in open dishes left unweighable and scarcely visible residues. The insignificant amount of the residues was a proof of the purity of the air, as well as of the acids. Neither acid gave a test for iron, and the nitric acid contained no chlorine even at the beginning of the operations.

Since the platinum still was very large, it was found more convenient to distil sulphuric acid from a small hard glass retort heated by a ring burner, immediately before it was needed. After three such distillations, a preparation was obtained which left no weighable residue upon the evaporation of any quantity used in the work.

All sulphuric acid used for drying was boiled with ammoniac sulphate.

In order to keep the air of the laboratory quite pure, during the greater part of the time neither volatile acids nor ammonia were allowed in the room devoted to the investigation, and all available precautions were taken against dust.

Indicators.—As is well known, the salts of most of the heavier metals are acid toward phenolphthalein and neutral toward methyl orange. The most important consequence of this relation has already been pointed out. When the former indicator was used, the slightly acidified solution was of course first freed from carbonic anhydride by long-continued heating upon the steam bath, and the end point was determined with pure caustic alkali. It is a noteworthy fact that methyl orange is useless in very concentrated solutions of sodic sulphate, the colour change becoming apparent only upon dilution. This indicator is naturally less serviceable in the presence of a strong colour like that of a copper salt. It is less sensitive with cupric sulphate than with cupric bromide. In such cases as these, colorimetric comparison can alone

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

afford accurate results; but even here the effect of a personal equation must be more or less perceptible.

Since the amount of either indicator used in any one case was not more than the thirtieth of a milligram, it could not have seriously influenced subsequent operations with the solution.

Water.—The distilled water taken hot from the tin-lined condenser around a steam drying oven contained no ammonia discoverable by Nessler's reagent, and in the first crude experiments this water was used without further treatment. After having been once more distilled in a platinum still, it appeared to be very pure. The first portions of the distillate were rejected, although no ammonia was found in them. The water left absolutely no trace of residue upon evaporation, even after long standing. Such doubly distilled water was used in the second series of experiments.

For the third series all the water used, even for minor operations, was distilled four times: first alone, then over alkaline potassic permanganate, next over acid potassic sulphate, and finally once more alone in the platinum still. Since this water was not different in any of its properties from the second preparation, the last refinements were probably unnecessary; and in later work water which had been distilled only twice was used.

The value of the present work has been largely increased by the unlimited supply of platinum ware placed at the disposal of the writer through the kindness of Professor Cooke. Because of the large size of some of the retorts and bottles, it was impossible to free these vessels from iron after the method of Stas. Accordingly they were digested alternately with strong hydrochloric and nitric acids until pure acid which had remained in them for days gave no test for iron after evaporation on the steam bath.

Smaller vessels were freed from iron in the usual manner, by treatment with the vapours of ammoniac chloride at a red heat, as well as with fused acid potassic sulphate. They were usually protected during ignition by an outer crucible, from which they were separated by a coil of platinum wire. Crucibles weighing 20 grms. rarely showed a variation of more than one-twentieth of a milligram between the weights taken before and after any ordinary operations, excepting when ignited with cupric oxide under conditions which will be explained later.

(To be continued).

NOTICES OF BOOKS.

Fuels: Solid, Liquid, and Gaseous. Their Analysis and Valuation. For the Use of Chemists and Engineers. By H. JOSHUA PHILLIPS, F.I.C., F.C.S. Second Edition, Revised and Enlarged. London: Crosby Lockwood and Son.

THE rise in the price of coal due to the action of parties hostile to each other, but jointly hostile to the public and to the industrial world, renders attention to its economic utilisation a matter of the foremost importance. Hence, such a work as the present deserves and will doubtless receive the appreciation of all extensive consumers of fuel.

As regards petroleum for use in this country, the author is not sanguine. He thinks, and with good reason, that if a good supply of cheap mineral oils were available, its market price would quickly be raised above the point at which it could be advantageously used. Of course, the furnaces, &c., specially constructed for its consumption would become mere dead plant, a prospect which effectually deters industrialists from any attempts at its use.

Concerning gaseous fuels the author says little. We have in this country no extensive supply of natural gas. Coal gas, at any rate when furnished by companies, is too

costly for use on the large scale, and "water-gas," except previously treated according to the Crookes patent, contains too much of the deadly constituent carbon monoxide to be consistent with safety. According to an analysis here given, it may contain 35.88 per cent.

Processes for desulphurising coal and coke are duly noted, including admixture with lime, chalk, soda, oxide of manganese, &c.; some of these processes were expected to yield at once a better coke and a purer gas. The author's opinion is that none of these methods have eliminated sufficient sulphur to justify their adoption on the large scale.

Among the more important additions made in the present edition, we notice methods for determining the ash of fuel. In coal and coke the ash is not merely a something to be subtracted from what would otherwise be the calorific value of the fuel, but it often interferes in a very annoying manner with the quality of the product to be obtained. Hence the metallurgist requires accurate and at the same time simple and expeditious methods for the analysis of his fuels. This want is well supplied in the work before us.

Chemists, engineers, &c., connected with metallurgical establishments or any works where fuel is extensively used, will find this manual of great service.

Gas Works; their Construction and Arrangement, and the Manufacture and Distillation of Coal Gas. Originally written by SAMUEL HUGHES, C.E. Re-written and much Enlarged by WILLIAM RICHARDS, C.E. Eighth Edition, Revised, with notices of recent Improvements. London: Crosby Lockwood and Son.

WHEN a technical work has reached its eighth edition the task of the reviewer is very much restricted. Still, we are compelled to point out one error, the more to be regretted on account of the wide circulation of the book. We refer to the favourable notice of Winsor or Windsor, whose real name was Winzer. This man gathered a knowledge of gas lighting from a memoir by Lebon, about ten years after the new illuminant had been practically introduced by Murdoch, came to England in 1802 or 1803, and described himself as the "discoverer, inventor, and patentee" of gas lighting. The fact is that he had contributed nothing whatever to the invention of gas, no more than to its manufacture. Our authors speak of his "extraordinary courage, perseverance, and zeal." These attributes, however, when employed in laying claim to the results of others generally receive less pleasant names. Possibly we may award to Winzer the somewhat questionable honour of having originated gas companies.

In Chapter III. we find carbon monoxide, or carbonic oxide, made to rank as a diluent of coal gas; but, on account of its fearfully poisonous nature we should place it upon the impurities. Our authors, though admitting its deadly character, do not consider it an impurity. It may be mentioned that the absence of sulphur compounds in coal gas is demanded more strictly in some Continental cities than in London.

On page 55 we are told that the hostile attitude of the coal interests to the public at large dates back to 1665, when the extortions of the dealers are characterised as having been excessive.

Attention is also drawn to the deterioration of coal by prolonged storage. We regret to find the word "caloric" occasionally used; we thought it had become obsolete even in its native country.

It appears that the iron oxide used for purification is often mixed with sawdust. This, we submit, must be disadvantageous if the spent mass is afterwards burnt in the kilns of sulphuric acid works, as it will be impossible to prevent the sulphurous acid given off from being more or less contaminated with carbonic acid.

Concerning test-papers, Twaddell hydrometers, alkali-meters, and test acid, we find the remarkable statement: "The only firm that supply them that we know of is A.

Wright and Co., Westminster." All these requisites can be obtained from any dealer in chemical apparatus.

The success of Cooper's patent for mixing lime with the coal before charging the retorts is here traced to the admission of a small quantity of air into the oxide purifiers. The advantages claimed by Cooper are admitted, but they are due to a different cause.

It is here said that the product saccharine was first obtained in the laboratory of the Beckton gas works.

The electric light is, of course, disparaged. Gas companies are told to seek improvements that the price of gas may be reduced, and to seek out new applications. This movement was already in progress, but the recent serious rise in the price of gas in which one at least of the London gas companies has indulged bids fair to put an end to gas cooking ranges. Many people who had introduced these useful appliances have found it necessary to lay them aside.

The work before us, though drawn up too much in the interest of gas companies, is undoubtedly ably written and useful.

The Construction of Gas Works Practically Described. By W. R. HERRING, Manager Huddersfield Corporation Gas Department. With specially prepared Plates, Illustrations, and numerous useful Tables. London: Hazell, Watson, and Viney.

THIS work has evidently been drawn up with great care by an author who has no less evidently a thoroughly practical acquaintance with his subject. As an official of a municipal gas establishment, he does not adopt the "company" tone so unpleasant to all persons who are not shareholders. The substance of the work, however, lies for the most part outside our cognisance.

As regards the temperature to which the retorts are heated, the author says that the modern practice is to use high temperatures so as to produce a maximum yield per ton of coal. He states subsequently that at all temperatures above 980° much of the olefiant gas—the most luminiferous constituent—is eliminated; consequently the high heats now in vogue mean a sacrifice of quality to quantity.

It appears, especially in these days when strikes and rumours of strikes are rife, necessary for gas works to keep a considerable quantity of coal in store; but, as Mr. Herring points out, coal stored for whatever purpose rapidly deteriorates to the extent of 30 or 40 per cent in six months. Here is a powerful argument in favour of the proposal to generate gas close to the pit's mouth, using the coal as soon as brought up. In any case it would be well to adopt the author's simple suggestion of covering the coal stores at gas works with waterproof sheeting to exclude rain.

The coal "brasses" are a nuisance in the gas manufacture, as, indeed, in all the uses of coal, domestic or industrial. Mr. Herring proposes to give the men who "trim" the coal a premium over and above their wages on each cwt. of "brasses" picked out. This is well as far as lumps are concerned; but some coal contains iron sulphide disseminated through its entire mass in such fine specks and films that picking out is impossible. Hence the gas engineer, like the metallurgist, finds it necessary to keep a sharp watch on the quality of his coal.

As far as we are able to judge, this work may be highly recommended.

Manual of Assaying Gold, Silver, Copper, and Lead Ores. By WALTER LEE BROWN, B.Sc. Fourth Edition, 1892. Chicago: E. H. Sargent and Co.

BROWN'S "Manual of Assaying" has evidently given universal satisfaction both in America and Europe, or it would certainly not have reached its fourth edition in nine years. This favourable opinion will, we think, be endorsed by a

experts who have used it as a book of reference, and beginners will find it a safe guide.

The difficulty of defining assaying as distinct from analysis the author disposes of by confining the former term to dry methods, and the latter to those methods which chiefly employ liquid reagents. The electrolytic method (for copper at least) is made to rank as an analysis. Others, we must remember, adopt a different definition: they call a process analysis "when the end aimed at is the recognition and determination of all the constituents of an ore, an alloy, &c."; but assay when merely the percentage of some one valuable constituent is to be ascertained.

To one point in Mr. Brown's definition both of assaying and analysis we may take exception. He defines assaying as that branch of *exact science* which enables us, &c., whilst analysis effects the same results, &c. Now we submit that assaying and analysis alike are not branches of *science*, but *industrial arts*, based upon the sciences chemistry and physics.

The prices of some of the more important and costly articles of apparatus are given both in American and in English money. We do not know whether in calculating these prices due attention has been given to the circumstance that the price of any piece of apparatus made in Europe is enhanced in the United States by the peculiar fiscal system of the latter country. It is very questionable what claim the assays of copper, tin, cobalt, nickel, &c., have to be retained in presence of the improved and accelerated analytical methods. With gold and silver the case is different. The author fully admits that for copper the dry methods are inaccurate.

Mr. Brown by the production of this work has decidedly earned the gratitude of all persons interested in metallurgy and mining. The only alteration which we can suggest is that he should take a broader point of view, and in place of the principal minerals likely to contain gold, silver, copper, &c., found in the United States, he should give those of the known world.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

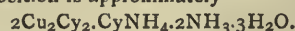
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 19, May 9, 1892.

Residual Life and the Functional Products of Tissues separated from the Living Being.—Arm. Gautier and L. Landi.—The authors show that vital processes still go on for a time in the tissues after the death of the entire animal.

On Sodium Trimethylcarbinol; Value of the Tertiary Alcohol Function.—M. de Forcrand.—A thermo-chemical paper not adapted for abstraction.

Action of Potassium Cyanide upon Ammoniacal Copper Chloride.—E. Fleurent.—The author has obtained long blue crystalline needles arranged in small tufts and of little stability, the ammonia rapidly escaping. Their composition is approximately—



The mother-liquor, after the escape of the ammonia, deposits fine green rectangular lamellæ, very stable, of the composition $2\text{CuCy}_2 \cdot \text{Cu}_2\text{Cy}_2 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$. These lamellæ are insoluble in water, but soluble in ammonia, from which they are deposited unchanged. They decompose at temperatures exceeding 100° . If treated with dilute acids they emit hydrocyanic acid and deposit cuprous cyanide. The solution from which these green crystals have been deposited, if set aside, yields lastly a mixture

of micaceous tablets and of other crystals which the author is examining.

Establishment of Fundamental Formulæ for the Calculation of the Moments of Maximum Inertia.—G. Hinrichs.—A purely mathematical paper.

Chemical Properties of Acetyl Fluoride and on its Analysis.—Maurice Meslans.—Water acts upon acetyl fluoride in an analogous manner to what it does upon acetyl chloride. Hydrofluoric and acetic acid are formed slowly and less energetically than in case of the chloride. If we treat the liquid acetyl fluoride with two or three volumes of cold water, the two liquids do not mix, but the fluoride disappears slowly. Potassa and soda in alkaline solutions quickly decompose acetyl fluoride, forming a mixture of alkaline fluoride and acetate. Quicklime introduced into a vessel filled with gaseous acetyl fluoride absorbs the gas, producing calcium fluoride and acetic anhydride. Gaseous ammonia reacts energetically upon liquid acetyl fluoride, producing a white crystalline mass, in which the microscope reveals the presence of two distinct substances. Aniline reacts powerfully upon acetyl fluoride, forming hydrofluoric acid and acetanilide melting at 115° . Absolute alcohol dissolves acetyl fluoride in every proportion, but the two substances do not react immediately. After prolonged contact in a closed vessel there are formed hydrofluoric acid and acetic ether, which may be separated on the addition of water. Amylic alcohol behaves in an analogous manner. Sodium amalgam and metallic sodium do not act sensibly upon liquid acetyl, but at dull redness sodium decomposes the gaseous fluoride with incandescence.

On Acid Pyrocatechine Antimonite.—H. Causse.—The compound in question is either a phenolic ether of antimonious acid or an acid pyrocatechine antimonite.

Action of Organic Acids upon the Acetylenic Carbides.—A. Béhal and A. Desgrez.—The acetylenic carbides, if strongly heated along with acetic acid, form instable compounds, which, in contact with water, are transformed into acetones. The reaction takes place in a sealed tube at 250° . The authors have operated upon cenanthylidene, caprylidene, butylmethylacetylene, and pentylmethylacetylene.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 74.

This issue does not contain any chemical matter.

Journal für Praktische Chemie.
New Series, Vol. xlv., Part 1.

Our Knowledge of the Oximes and the So-called Stereo-Chemistry.—Ad. Claus.—A reply to a controversial paper by Auwers and Meyer, which appeared in the *Berlin Berichte*.

Communications from the Chemical Institute of the University of Kiel.—These consist of a paper by C. Stoehr on the pyridine and piperidine-bases of the β -series, in which the poisonous character of β -methylpiperidine and β -ethylpiperidine is experimentally shown. The phenomena produced resemble those occasioned by conine.

On the So-called γ -Bromquinoline.—Hermann Decker.—Not adapted for useful abstraction.

The Addition of Sodium Acetacetic and Sodium Malonic Ethers to the Ethers of Unsaturated Acids.—A. Michael and O. Schulthess.—The authors communicate the results of their experiments on the addition of the former class of ethers to a series of ethers of the unsaturated polybasic fatty acids.

The Polymerisation of the Nitriles.—E. von Meyer.—The author controverts the views of Hanriot and Bouevault to be found in *Bull. Soc. Chimique*, li., p. 170.

Zeitschrift für Anorganische Chemie.
Vol. i., Part 2.

On a Series of Trihaloid Compounds of Cæsium.—H. L. Wells.—With an "Account of their Crystallographic Properties," by S. L. Penfield.—This paper appears also in the *American Journal of Science*, 1892.

Contributions to Quantitative Spectroscopic Analysis.—G. Kriess and H. Krüss.—This valuable memoir will be reproduced as nearly as possible in full.

The Sulphocyanides of some Ammoniacal Compounds of Chromium.—Otto Nordenskiöld.—After some introductory matter with reference to the researches of Morland, Reinecke, and Cleve, the author examines the salts of chromodiaminsulphocyanide-hydrosulphocyanic acid and their derivatives, especially the ammonium salt, its reaction with aniline, its iodide, the potassium salt and its iodide, the barium, ferric mercury, silver, and aniline salts, chromodiamindianilidorthorhodanideaniline sulphocyanide, the piperidine salt, the free acid, and the mercuric sulphide compound of chromodiamintrisulphocyanide. In the second part Prof. Nordenskiöld examines the trisulphocyanides and their derivatives. Experiments to substitute N_2O with methyl sulphide were not successful. The author has also attempted to obtain a cobalt compound corresponding to these chromium compounds. Crystals were obtained which are not analogous to the chromium compounds. A brief notice is given of a paper by Odin T. Christensen on the "Compounds of Chromammonium Sulphocyanogen."

A New Direct Separation of Chlorine, Bromine, and Iodine.—P. Jannasch and K. Aschoff.—The authors have adopted the following method for the separation and gravimetric determination of the three halogens. The solution containing weighed quantities of sodium chloride, potassium bromide, and potassium iodide (about 0.3 gm.) of each salt was placed in a distillatory flask (which the authors figure) diluted with water to a volume of 750 c.c., and acidified by the addition of 5 c.c. of dilute sulphuric acid. The dilution is necessary to prevent the simultaneous escape of hydrochloric and hydrobromic acids. They then add to the cold liquid a solution of 1 gm. sodium nitrate in 10 c.c. water, when the flask must be instantly closed. The contents are at once turned to a reddish-brown colour by the liberation of iodine. The outlet tube of the flask is introduced into a cylinder, as deep as possible, of the capacity of 500 c.c., containing a mixture of 50 c.c. pure soda-lye, and 50 c.c. hydrogen peroxide, and is closed with a cork having two perforations. Through the second aperture of the cork passes a second glass tube bent twice at right angles and plunging with its longer limb into a flask containing the necessary quantity of the mixture of hydrogen peroxide and soda-lye, in order to keep back any traces of iodine which may be carried over mechanically. The cylinder is kept cold by being placed in cold water. A current of steam is then passed into the flask through the tube *a*, (the one which is *not* bent twice), the contents quickly become hot, and violet-coloured fumes of iodine fill the empty space, condensing in part in crystals in the cold portion of the outlet pipe, and being subsequently absorbed in the receiver. In about fourteen minutes the vessel becomes perfectly colourless, showing the complete expulsion of the iodine. The cylinder is then cautiously removed, and the immersed end of the tube is well rinsed with the washing-bottle. Not until then is the current of steam interrupted. The contents of the receivers are then entirely poured into a porcelain capsule which is covered, and heated on the water-bath after the further addition of 50 c.c. of the hydrogen peroxide solution for the complete oxidation of any traces of sodium nitrite. After the lapse of some hours solution of silver is added, whilst stirring, to the alkaline liquid. The brown precipitate first formed disappears on stirring, with formation of silver iodide, and the addition of silver nitrate is continued until the dark colour of the precipitate no

longer changes to yellow. The liquid is then acidified with nitric acid and heated for some hours on the water-bath until the silver iodide has been completely deposited, when it is filtered hot, dried, incinerated, fused, and weighed. The liquid should not be allowed to become cold. For the separation of the bromine and chlorine existing in the flask, the acid liquid is made distinctly alkaline with soda-lye. When it has been concentrated to about 50 c.c. it is returned to the flask, and when cold mixed with 60 c.c. dilute acetic acid (1:3 water), and with a concentrated solution of from 1 to 1.5 gm. permanganate. The two receivers are then connected with the flask, and a current of steam is introduced. An increasing turbidity of the liquid appears, and yellowish-red vapours of bromine are given off. The current of steam must not be too strong, the better to effect the complete absorption of the bromine by the soda-lye in the receiver. The distillation takes about forty-five minutes when the apparatus is disconnected; the contents of the receivers are poured into a porcelain capsule and heated for a time as above directed. Lastly, the precipitation of the bromine was effected with a mixture of silver solution and nitric acid (10 per cent silver solution and concentrated nitric acid). The silver bromide is filtered off and further treated as directed for iodine. The chlorine remains in the flask. For its determination the excess of permanganate is first reduced by adding soda-lye and alcohol and applying heat. The precipitate of manganese is filtered off and washed with luke-warm water. The clear filtrate is acidulated with nitric acid and the chlorine precipitated with silver nitrate.

Examination of the Atomic Weight of Copper.—Th. W. Richards.—The mean result of seven series of determinations is $\text{Cu} = 63.605$.

MISCELLANEOUS.

Has Sulphur been Decomposed?—We mention, though not without strong doubts, the rumour that the elementary character of sulphur is in question. Dr. Gross is said to have been for many years engaged in exhaustive researches on this substance. He has communicated certain of his results at a meeting of the Physical Society of Berlin. Barium sulphide was fused in a silver crucible, and a powerful electric current was introduced by means of a platinum wire inserted in the melting mass. After some time it appeared that the barium had combined with the platinum to form a novel compound, whilst some 50 per cent of the sulphur had disappeared, leaving a corresponding quantity of a new substance in its place. Dr. Gross considers that sulphur is not an element, but the hydride of the new body. Several questions here suggest themselves, which it may be better to reserve, pending the appearance of further research on the question.

MEETINGS FOR THE WEEK.

- TUESDAY, 31st.—Institute of Civil Engineers, 8. (Anniversary).
 — Royal Institution, 3. "Some Aspects of Greek Poetry," by Prof. R. C. Jebb.
 — Society of Arts, 8. "Lustre Ware," by William De Morgan.
 THURSDAY, June 2nd.—Royal Institution, 3. "On Faust," by R. G. Moulton, M.A.
 — Royal, 4.30.
 — Royal Society Club, 6.30.
 — Chemical, 8. "Ethylene Derivatives of Diazo-amido Compounds," by R. Meldola, F.R.S., and F. W. Streetfield, F.I.C.
 FRIDAY, 3rd.—Royal Institution, 9. "Metallic Carbonyls," by Ludwig Mond, F.R.S.
 — Geologists' Association, 8.
 — Quaker Club, 8.
 SATURDAY, 4th.—Royal Institution, 3. "Some Modern Discoveries in Agricultural and Forest Botany," by Prof. H. Marshall Ward, F.R.S.

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NOTICE TO CONTRIBUTORS OF MEMOIRS.—Authors are reminded that the acceptance of memoirs and the days on which they are to be read are, as far as possible, determined by Organising Committees for the several Sections before the beginning of the Meeting. Memoirs should be sent to the office of the Association. Information about local arrangements may be obtained from the Local Secretaries, Edinburgh.

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THE CHEMICAL NEWS.

Vol. LXV., No. 1697.

NOTE ON THE SPONTANEOUS CONVERSION OF ISOPRENE INTO CAOUTCHOUC.*

By WILLIAM A. TILDEN, D.Sc., F.R.S.

ISOPRENE is a hydrocarbon which was discovered by Greville Williams many years ago among the products of the destructive distillation of indiarubber: Later, in 1884 (*Trans. Chem. Soc.*, xlv., 410), it was observed by myself among the more volatile compounds obtained by the action of a moderate heat upon oil of turpentine and other terpenes. It is a very volatile liquid, boiling at about 36°. Its molecular formula is C_5H_8 , and it forms a tetrabromide, $C_5H_8Br_4$, but no metallic derivatives, like the true homologues of acetylene.

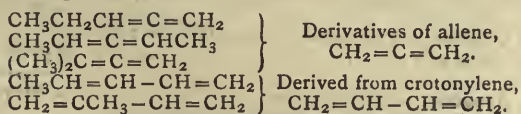
Bouchardat (*Comptes Rendus*, lxxvii., 654, and lxxix., 361 and 1117), observed that when isoprene is heated to a temperature near 300°, it gradually polymerises into a terpene which he called di-isoprene, but which is now usually called *dipentene*. This compound boils at 176°. A quantity of colophene similar to that which is produced by the action of heat upon turpentine is formed at the same time.

When isoprene is brought into contact with strong acids, aqueous hydrochloric acid for example, it is converted into a tough elastic solid, which has been examined by G. Bouchardat and by myself; it appears to be true indiarubber.

Specimens of isoprene were made from several terpenes in the course of my work on those compounds, and some of them I have preserved. I was surprised a few weeks ago at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In place of a limpid colourless liquid the bottle contained a dense syrup, in which was floating several large masses of solid of a yellowish colour. Upon examination this turned out to be indiarubber. The change of isoprene by spontaneous polymerisation has not to my knowledge been observed before. I can only account for it by the hypothesis that a small quantity of acetic or formic acid had been produced by the oxidising action of the air, and that the presence of this compound had been the means of transforming the rest. The liquid was acid to test paper, and yielded a small portion of unchanged isoprene.

The artificial indiarubber, like natural rubber, appears to consist of two substances, one of which is more soluble in benzene or in carbon bisulphide than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characters with a similar preparation from Para rubber. The artificial rubber unites with sulphur in the same way as ordinary rubber, forming a tough elastic compound.

The constitutional formula of isoprene is not known with certainty, but it must be selected from the five following formulæ:—



It is obvious that compounds such as these containing doubly-linked carbon may polymerise in a variety of

ways, and in the present condition of our knowledge of the constitution, even of isoprene, it would be idle to speculate as to which out of the numerous possible arrangements would correspond to the constitution of caoutchouc.

ESTIMATION OF NITROGEN.

By VINCENT EDWARDS, F.C.S.

IN a few remarks inserted in the *CHEMICAL NEWS*, lxx., p. 241, on the above subject, I fear I did not make myself sufficiently clear upon one point, which is, that when a sample is found by preliminary test to contain a fairly high amount of nitrate, the method will not succeed unless the usual modification (Scovell's) is carried out, or, in other words, the process will only answer with traces of nitrates along with ammoniacal and organic nitrogen.

I find that for the estimation of nitrogen in nitrates of soda and potash, the iron flasks are very convenient, economical and rapid, quite equalling in all but appearance the fancy sketches seen in some text-books. Care must be taken to try several blank determinations, as the iron filings give up some ammonia due to slow oxidation. Good quantities are 10 grms. of zinc grains, 5 grms. iron filings, $\frac{1}{2}$ grm. of nitre, 100 c.c. of 30 per cent solution of potash, and 50 c.c. of water. This is allowed to stand for one hour, 100 c.c. more water added, and the ammonia distilled off into standard acid.

Lawes' Works, Barking,
May 31, 1892.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 261).

Description of Analyses.—First Series.

It is evident from the most probable constant error in Hampe's work lay in the great hygroscopic power of cupric sulphate dried at 250°. A possible means of detecting such error existed in the use of the crystallised salt as a starting point. This salt was therefore coarsely powdered, dried to constant weight over a mixture of crystallised and partially dehydrated cupric sulphate, and analysed by electrolysis in the usual fashion. Although the crystalline powder must have contained occluded water, the quantity of copper found in several samples from different sources was much larger than that demanded by the old atomic weight, and closely approached the theoretical quantity based upon the new value.

In the third experiment the weight of water lost by heating the salt to constant weight in the manner described by Hampe (*loc. cit.*) was also determined, and this amount proved to be nearly three-tenths of a per cent less than it should have been according to any hypothesis. Since larger crystals of cupric sulphate exposed to air above the desiccating mixture already mentioned lost none of their lustre, and since the salt under these conditions comes to perfectly constant weight, it seemed highly probable that the apparent deficiency of crystal water was due to occlusion in the so-called anhydrous salt, and not to any previous efflorescence of the crystals.

The sulphuric acid produced during the electrolysis

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

† In this connection it may be noted that Hart and Crossdale have quite independently used the sulphuric acid thus formed as a basis of alkalimetric analysis. (*CHEM. NEWS*, lxiii., 93, 1891). The idea appears to be a good one.

* Paper read before the Philosophical Society of Birmingham, May 18, 1892.

was preserved in each case, and approximately determined by means of the first preparation of sodic carbonate; also afterwards by the evaporation of the solution of sodic sulphate. Since the manipulation was more or less imperfect, and the materials and water not quite pure, it is thought unnecessary to include these somewhat bulky data in full here, but the evidence which they furnished was conclusive upon one point. The percentage of acid was not equal to the complement of the other percentages. In other words, over one-tenth of a per cent of material had not been determined.

Percentage of—	Found.	Theory Cu = 63.60.	Theory Cu = 63.33.
Water	35.958	36.0695	36.109
Copper	25.455	25.4665	25.385
SO ₄	38.46±	38.464	38.506
Total.. ..	99.87	100.000	100.000

It is seen that we are dealing, not with infinitesimals, but with grave error, evident to the crudest analysis. The reason for the deficiency has already been suggested, but the proof is yet wanting.

The ratio between the copper and the sulphuric acid, or rather between the copper and sodic carbonate on the one hand, and sodic sulphate on the other, affords a new twofold basis for the calculation of the atomic weight of copper. This basis is entirely independent of the always uncertain weight of the cupric sulphate and the objectionable method of calculation from difference. The results correspond to the new atomic weight, but the complete discussion of this phase of the subject will be reserved until more definite data have been given. It is interesting to note that these comparatively crude experiments differ only by one or two units in the second decimal place of the result from the far more carefully executed work yet to be described.

Analysis of Cupric Sulphate.—First Series: Data and Results.

(Weights reduced to vacuum standard).

No. of Expt.	Weight cupric sulphate (cryst.).	Weight CuSO ₄ (250°) found.	Weight copper found.	Per cent water lost at 250°.	Per cent copper.
1.	2.8815	—	0.7337	—	25.462
2.	2.7152	—	0.6911	—	25.452
3.	3.4639	2.2184	0.8817	35.958	25.454
Average				35.958	25.455

Second Series.

Although from the earlier experiments it appeared that the deficiency in the sum of the analytical results might be explained by the hypothesis of the existence of water in the so-called anhydrous cupric sulphate, it was possible that at least a part of this deficiency might be due to experimental error. The next step of the research was therefore to start again upon a more refined basis. It was important, too, that some proof of the above mentioned hypothesis more definite than an indirect inference should be obtained. The clearest idea of the various operations may probably be acquired through a detailed statement of one of the experiments, and accordingly such a statement is given below.

Experiment 4.—The cupric sulphate (see p. 245), having been cautiously powdered in an agate mortar and dried to constant weight over the desiccating mixture already described, was gradually heated to 255° in a platinum crucible with a very closely fitting lid.

The crucible and contents gained in weight upon the balance pan at a rate of only one-tenth of a milligram. in four minutes, and hence the last weighing is without doubt sufficiently accurate. When the weight had thus become constant, 20 drops of strong pure sulphuric acid were added to the white powder, and the whole was kept

	Grms.
Weight of crucible + CuSO ₄ .5H ₂ O	= 23.36188
„ „ alone	= 20.30300
„ cupric sulphate in air	= 3.05888
Correction to vacuum (sp. gr. = 2.274) ..	= 0.00118
Corrected weight CuSO ₄ .5H ₂ O, in vacuum ..	= 3.06006
Weight crucible + CuSO ₄ dried for three hours at 255°	= 22.26243
Weight crucible dried for two hours more ..	= 22.26233

at a temperature of 365° for three and one-half hours in a suitable air bath composed of a nest of porcelain crucibles. An air thermometer was used in measuring the temperature.

	Grms.
Weight of crucible and contents	= 22.25905
The same, after re-heating for four hours with six drops more of H ₂ SO ₄	= 22.25900
Weight in air of cupric sulphate dried at 365° ..	= 1.95600
Weight in vacuum of cupric sulphate (sp. gr.* = 3.61)	= 1.95637

Loss of weight between 255° and 365° = 0.00333

The crucible and contents gained in weight even less rapidly than before.

This experiment shows that the so-called anhydrous cupric sulphate of Hampe loses about seventeen one-hundredths of a per cent of its weight when subjected to the temperature of the boiling point of mercury; a loss nearly equal to the deficiency which we are seeking to explain. The residual salt may be slowly dissolved in water without the need of very great caution. It gives a perfectly clear solution, which is neutral to methyl orange and does not deposit basic salt even upon indefinite standing. These facts alone show that the decrease in weight was not due to loss of acid, but a much more definite proof of this point is given later.

For electrolysis, the clear solution of the 1.95637 grms. of cupric sulphate was transferred to a large platinum crucible. This crucible had been previously coated inside with pure copper, washed with water and alcohol, and dried at 103°. The crucible was supported upon a platinum triangle in the interior of a large beaker, and was covered by a watch glass into which was fused the positive electrode. The wires conducting the current into the beaker were of platinum. The whole apparatus was covered with a large watch glass, which effectually excluded impurity. Several times before the conclusion of the electrolysis the drops adhering to the inner watch glass were washed back into the crucible by means of apparatus especially adapted for the purpose. After the maintenance for one hundred and twenty hours of a weak current (*Proc. Amer. Acad. Arts Sci.*, xxv., 202), the electrolysis was interrupted, and every trace of the acid in the crucible was washed as rapidly as was consistent with scrupulous care into a large platinum bottle. The crucible was then washed with pure alcohol, dried at 103°, and finally weighed.

	Grms.
Crucible + Cu before electrolysis (Bar. = 767; t° = 20°)	= 36.12120
Crucible + additional Cu after (Bar. = 750; t° = 20°)	= 36.90000
Apparent weight of copper	= 0.77880
Correction for change in temperature and pressure	= +0.00007
Correction to vacuum	= -0.00001

True weight of copper in vacuum = 0.77886

* This is a mean of the results of Hampe and Karsten.

	Per cent.
Percentage of copper in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	= 25'452
" " CuSO_4 dried at 255°	= 39'744
" " " " 250°	= 39'725
(Hampe)	= 39'811
Percentage of copper in CuSO_4 dried at 365°	= 39'811

Further comment here is unnecessary.

The earlier experiments had already shown approximately the equivalent ratio of sodic carbonate to copper. Accordingly a very little less than the amount of sodic carbonate corresponding to the data above was carefully weighed out from the second sample of this material, and the salt was ignited at a dull red heat until constant in weight. (See description of sodic carbonate, p. 260).

	Grms.
Weight crucible + Na_2CO_3	= 21'60095
" " alone	= 20'30260
" sodic carbonate in air	= 1'29835

Weight sodic carbonate in vacuum (sp. gr. = 2'466)	= 1'29880
--	-----------

The sodic carbonate was dissolved in water and poured into the very dilute solution of sulphuric acid which had been formed by the electrolysis. The lid of the crucible, as well as that vessel itself, was very thoroughly washed with water. On account of the great dilution of the liquid, carbonic anhydride was not at once set free, but upon warming for six or eight hours upon the steam-bath it was easily expelled. During this operation the platinum flask was of course suitably covered, a Gooch crucible being found most convenient for this purpose.

When gas evolution had long ceased, the solution was wholly transferred to a large platinum dish, and was evaporated on the steam-bath to a volume of about 50 c.c. The very slight excess of acid was then titrated by means of sodic hydroxide, using methyl orange as an indicator, and was found to require 0'09 c.c. of a decinormal solution for neutralisation. The probable error of the end point was not greater than one drop, or one ten-thousandth part of the sodic carbonate present.

	Grms.
Sodic carbonate weighed out	= 1'2988
" " added in titration	= 0'0005
" " required (in vacuum)	= 1'2993
Cupric sulphate taken ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	= 3'06006
Copper found in	= 0'77886

Per cent of SO_4 in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 38'439

Atomic weight of copper:

Na_2CO_3 : Cu = 106'108 : 63'606

In transferring the sodic sulphate from the evaporating dish to the capacious platinum crucible in which it was to be weighed, the precaution of washing with water which had been thoroughly boiled was absolutely essential to prevent the possibility of subsequent mechanical loss during evaporation. At best, the concentration of a solution in an open crucible over the steam-bath is an unsatisfactory operation, and accordingly for the third series a new method was devised. The water left the sodic sulphate very slowly; but in the end it evaporated so completely that after covering there was a scarcely audible decrepitation on heating the crucible to redness. The pure white sodic sulphate was finally fused at a bright red heat. During this last operation the salt occasionally became tinged with a slightly yellowish hue, due probably to a trace of iron from the platinum vessels; but the purest specimens remained wholly colourless. The salt lost only one or two-tenths of a m.grm. during the fusion. A drop of very dilute permanganate solution was not decolourised by the solution of the residual salt, showing that no reduction had taken place. A very small amount of insoluble residue, consisting of the apparently unavoidable impurity in the sodic carbonate together with any iron or copper which might be present, was determined in each case; and the amount was subtracted from the weight of sodic sulphate. Naturally, besides this, it is necessary to subtract the amount of salt corresponding to the acid added in titrating back and forth when determining the end point of the acidimetric reaction. This end point had been taken as the average of a number of readings. Below are the data of the experiment under discussion.

	Grms.
Weight of crucible + Na_2SO_4 (&c.)	= 18'67040
" " alone	= 16'92594
Uncorrected weight of Na_2SO_4	= 1'74446
Subtract weight of salt added in titration	= 0'00362
" " insoluble residue	= 0'00034
Corrected weight of Na_2SO_4 in air	= 1'74050
Correction to vacuum (Sp. gr. = 2'631)	= +0'00063
Weight Na_2SO_4 in vacuum	= 1'74113
Per cent of SO_4 in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	= 38'445
" " " " found above	= 38'439
Atomic weight of copper (if Na_2SO_4 = 142'166, from table):	
Weight Na_2SO_4 : weight Cu = 142'166 : 63'595.	

No copper was found in the solution of the sodic sulphate, and a minute trace only in the insoluble residue. The object of the second experiment of the series was

Analysis of Cupric Sulphate.—Second Series : Data. (Weights reduced to vacuum standard).

No. of Experiment.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ taken. Grms.	CuSO_4 (260°) taken. Grms.	CuSO_4 (360°) found. Grms.	Metallic copper found. Grms.	Sodic carbonate required.		Sodic sulphate found. Grms.
					Methyl orange. Grms.	Phenol- phthalein. Grms.	
4	3'06006	1'9597	1'95637	0'77886	1'2993	—	1'7411
5	2'81840	1'8048	—	0'71740	—	—	—
6	7'50490	4'8064	4'79826	1'90973	3'1859	3'1865	4'2679

Second Series.—Results.

No. of Experiment.	Water lost at 260°.	Additional loss at 360°.	Total per cent of water (360°).	Per cent of copper.	Per cent of SO_4 by Na_2CO_3 (average).	Per cent of SO_4 by Na_2SO_4 .
4	35'959	0'109	36'068	25'452	38'439	38'444
5	35'964	—	—	25'454	—	—
6	35'957	0'108	36'065	25'446	38'435	38'424
Averages ..	35'960	0'108	36'067	25'450	38'437	38'434

to determine whether the method of weighing cupric sulphate in a tightly covered crucible was an accurate one. The determination was in every respect modelled after the mode of procedure adopted by Hampe, a tightly-stoppered weighing-bottle being used to contain the salt. The result sufficiently confirmed the previous experiment. For later experiments a crucible was accordingly used, since the evaporation of sulphuric acid at high temperatures is much more feasible in such an apparatus. A mishap prevented the accurate determination of the acid.

For the third experiment a much larger amount of material was used, the method being essentially that of the first experiment. The large crucible of 150 c.c. capacity used for the electrolysis was not previously coated with copper. The end point of the acidimetric determination was taken with both phenolphthalein and methyl orange, the colour change with the latter indicator being rather unsatisfactory in the presence of so large an amount of dissolved substance. The amount of insoluble residue found in the sodic sulphate was only 0.0003 grm.; it contained no trace of copper. The results showed that little was to be gained by the use of larger quantities of substance, since the unavoidable errors of quantitative work were multiplied nearly in proportion to the quantities of material. Mechanical errors are at the present day inessential compared with the constant ones which complicate so many analyses. It is obvious that a far more accurate result could be obtained from four-tenths of a grm. of really anhydrous cupric sulphate than from 400 grms. of a substance still retaining nearly two-tenths of a per cent of water.

Adding in the small amount of water which is lost by cupric sulphate, between 25° and 365°, the percentage composition of the crystallised salt, as indicated by the second series of analyses, gives a much more satisfactory total result than before:—

Water lost at 25°	= 35.960
Additional water lost at 365°	= 0.108
Copper	= 25.450
Sulphuric acid radicle	= 38.436

Total .. = 99.954

Although greatly improved, the analysis still leaves much to be desired. Even in materials prepared with the described precautions, traces of impurity were manifest. In the last experiment, where a large amount of material was used, a few minute spots, which might have been arsenic, appeared on the clear surface of the electrolytic copper, and traces of a brownish colouration were observed upon the positive pole. Both of these impurities were so infinitesimal in amount that they could not reasonably have been expected seriously to affect the final result; but the thought that they might be responsible for a part of the remaining deficiency prompted the execution of a still more elaborate series of experiments. The data and results of the second series are appended.

(To be continued).

METHODS OF ANALYSIS OF DAIRY PRODUCTS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

BUTTER.

Microscopic Examination.

PLACE a small portion of the fresh sample taken from the inside of the mass on a slide, add a drop of pure sweet oil, cover with gentle pressure, and examine with a one-half to one-eighth inch objective for crystals of lard, &c.

Examine same specimen with polarised light and selenite plate without the use of oil.

Pure fresh butter will neither show crystals nor a parti-coloured field with selenite. Other fats melted and cooled and mixed with butter will usually present crystals and variegated colours with the selenite plate.

For further microscopic study dissolve 4 or 5 c.c. of the fat in 15 c.c. of ether in a test tube. Stopper the tube with cotton-wool loosely, and allow to stand twelve to twenty-four hours at room temperature (20°—25°). When crystals form at the bottom of the tube, they are removed with a pipette or glass rod or tube, placed on a slide, covered, and examined. The crystals formed by later deposits may be examined in a similar way.

Sampling.—If large quantities of butter are to be sampled, a butter trier or sampler may be used. The portions thus drawn, about 500 grms., are to be perfectly melted in a closed vessel at as low a heat as possible, and when melted the whole is to be shaken violently for some minutes till the mass is homogeneous. A portion is then poured into a vessel from which it is to be weighed out for analysis, and should nearly or quite fill it. This sample should be kept in a cold place till analysed.

Determination of Water.—1.5 to 2.5 grms. are dried to constant weight at the temperature of boiling water in a dish with flat bottom, having a surface of at least 20 c.m.².

The use of clean dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom is employed.

Determination of Fat.—The dry butter from the water determination is dissolved in the dish with *absolute* ether or with 76° benzene. The contents of the dish are then transferred to a weighed Gooch filter with the aid of a wash bottle filled with the solvent, and are washed till free from fat. The crucible and contents are heated at the temperature of boiling water till the weight is constant. The weight of fat is calculated from the data obtained.

Substitute Method for Fat.—Water may be determined by drying the butter on asbestos or sand, and the fat extracted by *anhydrous alcohol-free* ether in an extraction apparatus. The extract, after evaporation of the ether, is heated to constant weight at the temperature of boiling water and weighed.

Determination of Casein and Ash.—The crucible containing the residue from the fat determination, consisting of casein and ash, is covered and heated gently at first, gradually raising the temperature to just below red heat. The cover may then be removed, and the heat continued till the contents of the crucible are white. The loss in weight of the crucible and contents represents casein, and the residue in the crucible, mineral matter. In this mineral matter, dissolved in water slightly acidulated, chlorine may be determined gravimetrically with silver nitrate, or volumetrically, using potassium chromate as indicator.

Estimation of Salt (NaCl).

Volumetric Method.—The amount of the butter or butter substitute to be taken is from 5—10 grms.; weigh in a counterpoised beaker glass. The butter (fresh from the refrigerator) is placed in portions of about 1 grm. at a time in the beaker, these portions being taken from different parts of the sample. By this means a reasonably fair sample of the whole is obtained.

The given quantity having been weighed out, it is removed from the pan.

Hot water is now added (about 20 c.c.) to the beaker containing the butter, and after it has melted the liquid is poured into the bulb of the separating apparatus. The stopper is now inserted, and the contents shaken for a few moments.

After standing until the fat has all collected on top of the water, the stop-cock is opened, and the water, containing most of the salt, is allowed to run into an Erlenmeyer flask, being careful to let none of the fat globules pass.

Hot water is again added to the beaker, and thence

poured into the separatory apparatus, the bottle well shaken, and the foregoing process is repeated from ten to fifteen times, using each time 10 to 20 c.c. of water.

The resulting washings contain all but a mere trace of the NaCl originally present in the butter.

Estimation of NaCl in Filtrate.—The chloride of sodium is now determined in the filtrate by a standard solution of AgNO₃, using a few drops of a saturated solution of potassium chromate as indicator.

Specific Gravity.

Weight of Flask.—Use a small specific gravity flask of from 25 to 30 c.c. capacity. The stopper should be bevelled to a fine edge on top, and the lower end should be slightly concave to avoid any trapping of air. The flask is to be thoroughly washed with hot water, alcohol, and ether, and then dried from thirty minutes to one hour at 100°. After cooling in a desiccator the weight of the flask and stopper is accurately determined.

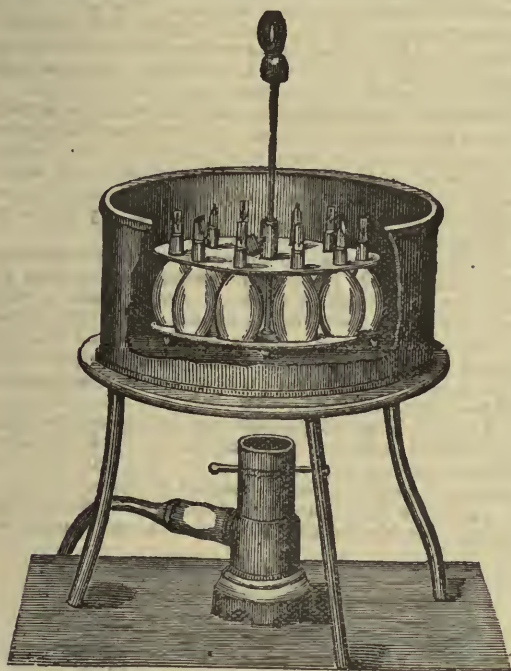


FIG. 1.

Weight of Water.—The flask in an appropriate holder (Fig. 1), conveniently made of galvanised iron, is filled with freshly boiled and still hot distilled water, and placed in a bath of pure, very hot, distilled water in such a way that it is entirely surrounded by the liquid with the exception of the top.

The water of the bath is kept in brisk ebullition for thirty minutes, any evaporation from the flask being replaced by the addition of boiling distilled water. The stopper* is then inserted, the flask removed, wiped dry, and after it is nearly cooled to room temperature, placed in the balance and weighed when balance temperature is reached. A convenient size of holder will enable the analyst to use eight flasks at once. The temperature at which water boils in each locality may also be determined; but unless at very high altitudes, or on days of unusual barometric disturbance, the variations will not be great, and will not appreciably affect the results.

* The stopper should be kept for a few minutes before use in hot distilled water.

ALTERNATE METHOD OF ESTIMATING THE WEIGHT OF WATER IN FLASKS.

Computation by the Formula of Landolt.

Formula for calculating volume V, in c.c., of a glass vessel from the weight P of water of temperature *t* contained therein, and the volume V' at any other temperature *t'* (from Landolt and Börnstein's "Physical-Chemical Tables," p. 39, Table 17):—

$$V = P \frac{\rho}{d}$$

$$V' = P \frac{\rho}{d} [1 + \gamma (t' - t)]$$

ρ = weight (in brass weights) of 1 c.c. H₂O in vacuo; see formula Table 3. (This is so nearly 1 that it will not

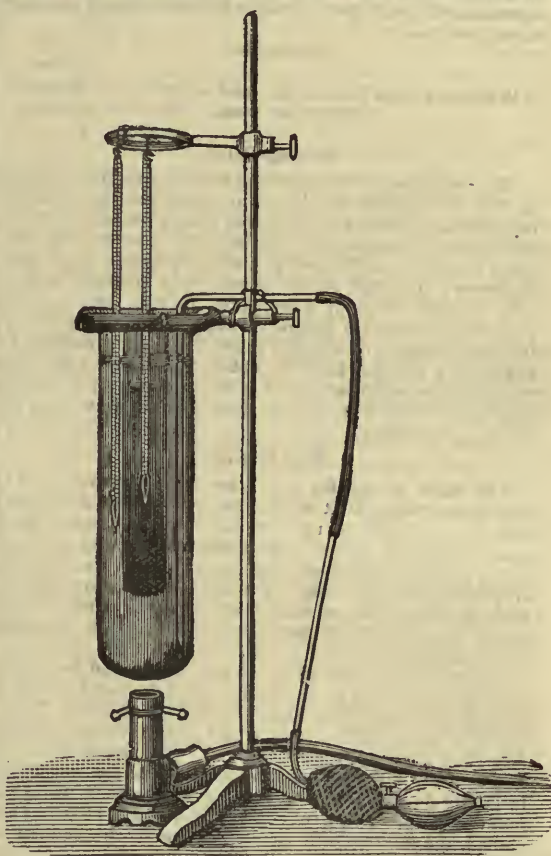


FIG. 2.]

affect the result in the fifth place of decimals, and may therefore be disregarded). Hence the formula stands:—

$$V' = P \frac{1}{d} [1 + \gamma (t' - t)]$$

d = density of water at temperature *t* (see Table 12).

γ = 0.000025, the cubical expansion coefficient of glass.

From this volume the weight of the water may be readily obtained by referring to Tables 13 and 13a.

Weight of Fat at Water-Boiling Temperature.—The flask is emptied of its water, rinsed with alcohol and ether, and dried again for a few minutes at 100°. It is then filled with the dry, hot, fresh-filtered fat, which should be entirely free from air bubbles.

The stoppered flask is then replaced in the water-bath,

kept for thirty minutes at the temperature of boiling water, removed, and treated as above. The weight of fat having been determined, the specific gravity is obtained by dividing it by the weight of water previously found.

Example.

	Grms.
Weight of flask No. 22, dry.. ..	10.0197
" " " plus water	37.3412
" " water	27.3215
" flask No. 22, plus fat	34.6111
" fat	24.5914
Specific gravity = $24.5914 \div 27.3215 = 0.90008$.	

The weight of the flask dry and empty, and the weight of water at 99° to 100° contained therein, may be used constantly if great care be taken in handling and cleaning the apparatus.

Example.

	Grms.
Weight of flask No. 10, dry and empty ..	10.0028
" " after three weeks' use ..	10.0030

Melting-Point.

The apparatus for determining the melting-point (shown in Fig. 2) consists of (1) an accurate thermometer for reading easily tenths of a degree; (2) a cathetometer for reading the thermometer (this may be done with an eye-glass if held steadily and properly adjusted); (3) a thermometer; (4) a tall beaker glass, 35 c.m. high and 10 c.m. in diameter; (5) a test-tube, 30 c.m. long and 3.5 c.m. in diameter; (6) a stand for supporting the apparatus; (7) some method of stirring the water in the beaker, for example, a blowing bulb of rubber, and a bent glass tube extending to near the bottom of the beaker; (8) a mixture of alcohol and water of the same specific gravity as the fat to be examined.

Manipulation.

The disks of the fat are prepared as follows:—The melted and filtered fat is allowed to fall from a dropping tube from a height of 15 to 20 c.m. on to a smooth piece of ice floating in water. The disks thus formed are from 1 to 1.5 c.m. in diameter, and weigh about 200 m.grms. By pressing the ice under the water the disks are made to float on the surface, whence they are easily removed with a steel spatula, which should be cooled in the ice water before using.

The mixture of alcohol and water is prepared by boiling distilled water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot, the water is poured into the test-tube already described until it is nearly half full. The test-tube is then nearly filled with the hot alcohol. It should be poured in gently down the side of the inclined tube to avoid too much mixing. If the tube is not filled until the water has cooled, the mixture will contain so many air bubbles as to be unfit for use. These bubbles will gather on the disk of fat as the temperature rises, and finally force it to the top of the mixture.

The test-tube containing the alcohol and water is placed in a tall beaker containing water and ice. The disk of fat is dropped into the tube from the spatula, and at once sinks until it reaches a part of the tube where the density of the alcohol water is exactly equivalent to its own. Here it remains at rest and free from the action of any force save that inherent in its own molecules.

The delicate thermometer is placed in the test-tube and lowered until the bulb is just above the disk. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disk, the thermometer is moved from time to time in a circularly pendulous manner. A tube prepared in this way will be suitable for use for several days; in fact, until the air bubbles begin to attach themselves to the disk of fat. In no case did the two liquids become so thoroughly mixed as to lose

the property of holding the disk at a fixed point, even when they were kept for several weeks.

In practice, owing to the absorption of air, it has been found necessary to prepare new solutions every third or fourth day.

The disk having been placed in position, the water in the beaker glass is slowly heated and kept constantly stirred by means of the blowing apparatus already described.

When the temperature of the alcohol water mixture rises to about 6° below the melting-point, the disk of fat begins to shrivel, and gradually rolls up into an irregular mass.

The thermometer is now lowered until the fat particle is even with the centre of the bulb. The bulb of the thermometer should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotary movement should be given to the thermometer bulb, which might be done with a kind of clockwork. The rise of temperature should be so regulated that the last 2° of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so, the reading of the thermometer is to be made. As soon as the temperature is taken, the test-tube is removed from the bath and placed again in the cooler. A second tube, containing alcohol and water, is at once placed in the bath. The test tube (ice water being used as a cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum about 1.5° above the melting-point of the fat under examination.

Working thus with two tubes, about three determinations can be made in an hour. After the test-tube has been cooled the globule of fat is removed with a small cup attached to a wire before another disk of fat is put in.

The distilled water in which the piece of ice floats, on which the disks are made, should be recently boiled to free it of all air particles. It is important that the disks be free from air bubbles.

The edge of the disk should not be allowed to touch the sides of the tube. This accident rarely happens, but in case it should take place and the disk adhere to the sides of the tube, a new trial should be made.

Triplicate determinations should be made, and the second and third results should show a near agreement.

Example.

Melting-point of sample of butter 6372 (No. 3):—

	Degrees C.
1	33.15
2	33.05
3	33.00

(To be continued.)

CONTRIBUTIONS TO QUANTITATIVE
SPECTRAL ANALYSIS.

By G. KRÜSS and H. KRÜSS.

THE methods of spectrophotometry or quantitative spectral analysis have of late years been increasingly used both in analysis and in the decision of theoretical questions. Quantitative spectral analysis presents a wide field both in organic and inorganic chemistry, and we hope that the following communications may be of some use in analytical practice:—

1. Comparison of the Various Methods of Spectroscopic
Quantitative Analysis.

One of the chief conditions for obtaining good results in such determinations is working with a spectrum a

pure as possible—that is, with the smallest practicable widths of slit. The diminution of the width of the slit, however, has its limits, since the edges of the slit, however carefully ground, are never mathematical right lines. Still, with well-made apparatus, the width of the slit may be reduced to 0.003 or 0.004 m.m. without the observation being disturbed by the appearance of transverse bands in the spectrum. In opposition to the advantage due to the purity of the spectrum comes the limitation of light owing to the reduced width of the slit. In quantitative spectroscopic work we have to arrange that as much as possible of the light falling upon the slit may reach the eye of the observer, and that a relative maximum of light reaches the slit. The latter point may be attained on whatever principle we are working. A comparison between the two methods, that of Vierordt with a symmetrical double slit and that of the polarisation spectro-photometric procedure, shows that Vierordt's method enables us more perfectly to work with a pure spectrum.

The authors show that all the polarisation spectro-photometers have a feeble luminosity, and therefore, the quantities of incident light being equal, require a greater width of slit than Vierordt's double-slit spectro-photometer.

This defect may be remedied by illuminating the slit, if practicable, by means of an electric light.—*Zeitschrift für Angew. Chemie.*

A METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. BROWNING.

AT the suggestions of Prof. F. A. Gooch, and following the general mode of procedure laid down in his paper (*Am. Chem. Jour.*, ix., p. 33) upon the separation of sodium and potassium from lithium by the action of amyl alcohol on the chlorides, I undertook a series of experiments looking toward the separation of strontium from calcium by the action of amyl alcohol on the nitrates. On boiling several portions of the so-called chemically pure calcium and strontium nitrates with amyl alcohol, nearly complete solubility was observed in case of the calcium salt, while corresponding insolubility seemed to be characteristic of the strontium salt, and these results seemed to warrant proceeding with the work.

For the quantitative tests to be described, standard solutions of specially purified strontium and calcium nitrates were prepared. In general the preparation was effected by precipitating a soluble salt of either element with ammonium carbonate in the presence of ammonium chloride, washing thoroughly with boiling water, dissolving in the least possible amount of nitric acid, and making up to measure. In the earlier experiments other methods of purification were used, such as the precipitation of the strontium nitrate by alcohol, and in case of the calcium salt the preparation of the nitrate from the carbonate precipitated by ammonium carbonate from a solution of calcium sulphate. The method first described, however, gave satisfactory results, the spectroscope failing to show in the product thus obtained any trace of intermixture of calcium and strontium salts, or the presence of any other appreciable impurity. In the determination of the standards of these solutions definite amounts were drawn off from burettes into counterpoised beakers or crucibles (according as the method of determination was by precipitation or evaporation) and weighed as a check on the burette reading. The strontium nitrate in each portion was converted into the sulphate, either by precipi-

tation in the presence of alcohol, or by evaporating and igniting, these methods yielding results closely agreeing. The calcium was determined by evaporation with sulphuric acid. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon strontium nitrate alone. Accordingly several amounts of the strontium salt were measured from a burette into counterpoised Bohemian beakers of about 100 c.m.³ capacity and weighed. The water was then evaporated over a water bath, and the dry salts dissolved in a few drops of water and boiled with 30 c.m.³ of amyl alcohol, that amount being determined upon for convenience. Care should be taken not to add more than the necessary amount of water to dissolve the salt, inasmuch as the presence of much water delays the process (it being necessary to expel all the water before the amyl alcohol can do its work) and tends to cause spattering due to the superheating of the water and consequent sudden generation of steam under the alcohol. It has been my experience that in the presence of a few drops of water the boiling goes on quietly, the water escaping easily through the amyl alcohol, so that in the course of a few minutes the alcohol reaches its normal boiling temperature (128—130° C.). In order that the inflammable fumes of the alcohol might not reach the flame during the boiling, the beaker was placed upon a piece of asbestos board about 15 c.m. square. When the temperature of the alcohol reached its normal boiling point (128—130° C.), as shown by a thermometer, the beaker was removed and the strontium nitrate filtered off upon an asbestos felt in a perforated platinum crucible, the crucible and felt having been previously dried and weighed.

The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a ground glass plate. The last traces of strontium nitrate were removed from the beaker by washing with small amounts of previously boiled amyl alcohol contained in a wash bottle, the mouthpiece of which consisted of a small chloride of calcium tube passing through the stopper and drawn out and plugged at the lower end with cotton to exclude particles of the calcium salt from the alcohol. By this device the introduction of moisture into the amyl alcohol was guarded against. The crucible containing the strontium nitrate was placed in an air bath and heated to 150° C. to drive off all amyl alcohol, and weighed. A constant weight was obtained uniformly in one treatment. Series I. contains the results of these experiments, the strontium being calculated as oxide.

Series I.

	StrO taken. Grm.	StrO found. Grm.	Loss. Grm.
1. . . .	0.1229	0.1220	0.0009
2. . . .	0.1231	0.1221	0.0010
3. . . .	0.1230	0.1219	0.0011
4. . . .	0.1227	0.1213	0.0014

These results suggested a possible solubility of the strontium salt, and accordingly experiments were made to test this point. Amounts of strontium nitrate closely agreeing with those above were taken and treated in the same manner. The filtrates amounting, without the washings, to about 25 c.m.³ were evaporated to dryness. The residue was ignited to burn off organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness, and weighed. In two cases the residue of strontium sulphate was found to contain of the oxide respectively 0.0009 gm. and 0.0010 gm. As will be seen, the solubility of the strontium nitrate averages about 0.0010 gm. of the oxide to 30 c.m.³ of amyl alcohol used. The exact extent of this solubility depends, of course, upon the amount of amyl alcohol remaining after boiling; and, since the source of heat is removed as soon as the normal boiling temperature of the alcohol is reached, very little decrease in the volume of the previously boiled alcohol results. On measuring the amounts

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xliii., January, 1892

of the alcohol remaining in several experiments I found them to approximate closely to 25 c.m.³. It seemed justifiable, therefore, to add as a correction to the apparent amount of strontium oxide found 0.0010 grm. for every 25 c.m.³ of amyl alcohol remaining, or for every 30 c.m.³ originally taken. Experiments were also made to determine whether the strontium nitrate might have been at all broken down in the process of boiling and heating, so that some strontium might be present in the final residue in the form of oxide or nitrite. In two of these experiments portions of strontium nitrate left by the treatment with amyl alcohol were dissolved, precipitated as the sulphate and weighed as such, and the results of these experiments (5 and 6) go to show that the composition of the strontium nitrate is not appreciably changed in the process of separation and drying. In certain other experiments directed to the same end, the residues of the process of separation were, after weighing and drying, treated with a drop of nitric acid, and again dried at 150° C. and weighed. These tests (7 and 8) confirm the indications of the previous experiments. Finally, a third experiment was made upon strontium nitrate dried at 150° C. to see what decomposition might result by heating to temperatures somewhat higher than 150° C.,—the temperature at which the residues of the previous experiments had been dried. The result shows that the loss in the twenty-five degrees above 150° C. is exceedingly slight.

	Grm.
(5) { Sr(NO ₃) ₂ calculated as SrO	0.1219
{ The same dissolved and precipitated as	
{ SrSO ₄ calculated as SrO	0.1219
(6) { Sr(NO ₃) ₂ calculated as SrO	0.1213
{ The same dissolved and precipitated as	
{ SrSO ₄ calculated as SrO	0.1214
(7) { Sr(NO ₃) ₂ calculated as SrO	0.1228
{ The same dried at 150° C. after adding a	
{ drop of HNO ₃	0.1228
(8) { Sr(NO ₃) ₂ calculated as SrO	0.1239
{ The same dried at 150° C. after adding a	
{ drop of HNO ₃	0.1239
(9) { Weight of Sr(NO ₃) ₂ dried at 150° C. ..	0.2482
{ Weight of the same portion dried at 165° C.	0.2480
{ Weight of the same portion dried at 175° C.	0.2478

When calcium nitrate was treated in a similar manner by boiling with amyl alcohol the mass of the salt dissolved, but minute portions separated out on the bottom or sides of the beaker. Such residues were, however, very small, and on weighing were found not to exceed 0.0003 grm. or 0.0004 grm. of the oxide. In several instances this insoluble residue was washed thoroughly with ethyl alcohol, dissolved in water, tested before the spectroscopic and found to give the characteristic calcium spectrum. All experience pointed to the fact that the formations of the residue was due to some very slight change of composition of the calcium nitrate. On one or two occasions the acidified solution of the residue appeared to reduce a drop of an extremely dilute solution of potassium permanganate, and this action suggested the presence of a nitrite. Treatment of this residue with nitric acid and subsequent evaporation of the excess of acid failed, however, to leave the calcium salt in a condition to be dissolved by amyl alcohol.

It is possible, therefore, that the real cause of insolubility is to be sought in the oxidation of the amyl alcohol and consequent formation of an organic acid, and, subsequently, of the corresponding calcium salt, but the amounts of the residue were so extremely small that it was not practicable to solve this question at once exactly and satisfactorily without directing attention too far from the main issue. Moreover, the error introduced by this peculiar behaviour of the calcium salt proved to be insignificant in its effects upon the quantitative determination of the calcium, and accordingly it was disregarded in the subsequent tests.

(To be continued.)

NOTICES OF BOOKS.

Watts's Dictionary of Chemistry. Revised and entirely Re-written. By H. FORSTER MORLEY, M.A., D.Sc., and M. M. PATTISON MUIR, M.A. Assisted by Eminent Contributors. In 4 volumes, Vol. III. London and New York: Longmans, Green, and Co., 1892. Large 8vo., pp. 856.

THIS volume extends from indigocarboxylic acid to phenyltetrazolecarboxylic acid, and comprises a number of exceedingly important articles, nearly all characterised by fulness of detail, clear arrangement, sound general views, and remarkable brevity of expression. Particular attention is due to the memoir on the "Periodic Law" by Douglas Carnegie. The writer notices the memoir produced in 1862 by Béguyer de Chancourtois, which, though published in the *Comptes Rendus*, strangely failed to attract public attention even in France until disinterred by Lecoq de Boisbaudran. The claims of Newlands are admitted, but with the reservation, that his law "was retrospective rather than phopetic." It is also conceded that the periodic law was nothing else than a generalised and developed form of the law of octaves, the conceptions underlying both laws being practically identical." The respective contributions of L. Meyer, of Hartley, Carnelley, Prudhomme, Watts, Roberts-Austen, and others to the theory are duly appreciated. Mendeleeff's views on the nature and origin of the elements are briefly noticed. It may here suffice to say, that the great Russian chemist is not favourable to the idea of the origin of the elements by a process of evolution.

Prof. H. E. Armstrong, F.R.S., contributes an article on isomerism, in which the varied and fluctuating connotations of the terms isomerism, polymerism, metamorphism, is pointed out. Especial reference is made to the use of these terms by Wanklyn, Kekulé, Tilden, McGowan, and others. Attention is here given to the arrangement of atoms in space according to the hypothesis of Van 't Hoff and Le Bel.

Isomorphism is discussed at considerable length and with great ability by Dr. Hutchinson. The relations known as polymorphism, morphotropy, isomorphotropy, and isogonism are successively expounded.

Ozone is ably discussed by Mr. Shenstone, of Clifton College. In these days, when it has been proposed to re-name this substance "electric gas," it may be useful to remind the world that ozone may be produced without the aid of electricity. It may also grieve some persons to learn that, according to Schöne, the presence of ozone in the atmosphere is still not proven. Antozone, which at one time attracted no little attention, is now considered to be simply hydrogen peroxide.

A suggestive and elaborate paper is that on the rare metals from the pen of W. Crookes, F.R.S. The author shows the complexity not merely of the crude minerals from which the so-called rare earths have been obtained, but in many cases even of the earths themselves. He suggests that these earths when they have been split up as far as possible, may be found to contain nearly sixty unknown bodies. Before any such substance can be recognised as elementary it must, Mr. Crookes suggests, be submitted to a more severe scrutiny than any body of this class has yet undergone. Pending the completion of this scrutiny he recommends that they should be designated as "quasi- or meta-elements,"—aggregates intermediate in rank between the molecules with which we have to deal in chemical reactions and the ultimate atoms.

Here the reader may compare the section on the molecular constitution of bodies supplied by Prof. J. G. Thomson, F.R.S.

The great difficulty to be encountered by the editors of, and to a less degree by the contributors to, such works as the present, consists in the continued stream of discoveries which supplement and sometimes modify or even

cancel a part of our former knowledge. The work when complete will be simply invaluable.

A Practical Introduction to Chemistry: being the Practical Introductory Course of Work in Use at Clifton College. By W. A. SHENSTONE, Lecturer on Chemistry in Clifton College. With Illustrations. New and Revised Edition (Third Edition). London and New York: Longmans, Green, and Co., 1892.

CONCERNING this book, there has occurred a slight irregularity which has for the moment puzzled us, and has, we fear, occasioned annoyance to the author.

A few weeks ago we received from the publishers a copy as of a "new edition," but bearing the date 1887. This was reviewed in our issue of May 13. Now, however, the real "new and revised edition" of the present year has reached us—the "third edition" as it is called in the introduction. This we have now accordingly the pleasure of examining. We find that it extends to 120 pages in place of 101 pages, as in the former edition. It opens with instructions on cutting and bending glass, a subject on which Mr. Shenstone can speak with recognised authority. It then treats of the balance and its use. The former edition commenced with the lessons to be learnt from the phenomena of burning, and gave less complete information on glass-working and the balance in the form of appendices.

The section on "burning" has been improved. The experiment showing that air will burn in an atmosphere of coal gas is calculated to prove very instructive. In fact, most of the operations recommended are well planned to cause the pupil to observe and to understand what he observes. The illustrations will be found neater and clearer than those in the former edition or editions.

The entire work, it will be found, contains no reference to examinations, and no advice to pupils supposed to be preparing for such deceptive ordeals. Nor did we in our brief and, under the peculiar circumstances, somewhat perfunctory notice of the second edition assert or even insinuate to the contrary. We merely raised the general question whether our exceptional number of elementary manuals stands in any causal connection with our national system of education. On the very contrary, we think that Mr. Shenstone's pupils are to be congratulated on the rational character of their course of training, and we wish his work could be substituted for some dozen others which we have had the pain of reading through.

Les Matières Grasses, Caractères, Falsifications, et Essai des Huiles, Beurre, Graisses, Suifs, et Cires. ("Fatty Matters: Characters, Falsifications and Assay of Oils, Butters, Fats, Tallows, and Waxes.") By Dr. GEORGES BEAUVESSAGE. Paris: Librairie J. B. Baillière et Fils, 1891. 16mo., pp. 324.

THIS volume pertains to a series now being issued by the publishers under the title "Bibliothèque des Connaissances Utiles," and treats of a most important class of substances,—a class interesting both on account of their many applications in the arts and of the varied and ingenious frauds of which they are the subject.

The author begins by drawing a distinction between fatty matters and fats. The latter are definite proximate principles of a known and fixed composition, ethers of glyceryl. The fatty matters, on the contrary, are variable mixtures of such principles. As the physical characters of the fats he mentions their condition as liquid or solid, their melting and congealing-points, which, curiously enough, are not in all cases absolutely identical, a phenomenon due in part to their feeble conductivity for heat, their specific gravity, and their solubility. Secondary physical properties which, however, have often to be taken into consideration in determining the nature of a specimen, are their fluidity, their refractive action, their coefficient of expansion, and their electric conductivity.

The methods of ascertaining these properties are fully and carefully described. In taking the specific gravity of an oil he recommends Regnault's bottle, and the areo-thermic balance of Dalican and Eudeville. This apparatus, as here figured, seems to be exactly identical with the Mohr-Westphal balance, so well-known in the laboratory.

The cohesion-figures of Chatin and the diazometer of Rousseau are also described. For determining the relative fluidity of oils the author recommends Barbey's exometre. For ascertaining the refractive action of oils the author mentions the Abbe refractometer and the oleorefractometer of Amagat and Ferdinand Jean, which requires for comparison a standard oil prepared by F. Jean, the refraction of which is null. Jean has also devised a special instrument for applying the Maumené test, the difference of temperature of an oil before and after treatment with sulphuric acid.

The examination of cod-liver oil takes a prominent place. We regret to find that the author seems to prefer the brown oils, the colour of which is due simply to the incipient decomposition of the nitrogenous tissues. It is doubtless true that pale oils artificially bleached have lost their medicinal value, but this is no argument against the natural pale oils obtained from livers which have had no time to putrefy. The detection of the sophistications of oils is rendered extremely difficult by the rarity of absolutely genuine specimens for comparison.

Butters, fats, and tallows, form the subject of Part III. In deciding upon the character of a butter great weight is laid upon its refractive power. Abbe's refractometer is regarded as inapplicable on account of the difficulty of keeping the sample melted at a constant temperature, whilst the apparatus of Amagat and F. Jean is of easy use. By means of this instrument the deviation of pure butter of the best quality is $+35^{\circ}$, that of oleomargarine only $+5^{\circ}$, that of cotton-oil $+20^{\circ}$. Lard, suets, &c., give — deviations. Thus the detection of these frauds is comparatively easy.

The colouration of butters with annatto must be pronounced a disgusting fraud, in view of the fact that this dye-ware is often worked up with stale urine, and has been found swarming with microbia.

Of all the fatty matters added to or used as substitutes for cow-butter the most to be approved is cocoanut butter, which in taste is scarcely distinguishable from the product of the cow, and is certain to be free from morbid micro-organisms. Tallows, it is shown, may contain some of the earlier stages of the dreaded tape-worm, *i.e.*, the cisticerci.

The fourth part of the book treats of waxes, animal, vegetable, and mineral.

This book, small as is its compass, is extremely rich in useful matter. Not merely the most trustworthy analytical processes, but the properties of the oils and fats, are clearly and accurately described. It must be strongly recommended both to analysts and to chemical industrialists.

Explosives Act, 1875 (38 Vict., c. 17).—Sixteenth Annual Report of Her Majesty's Inspectors of Explosives, being their Annual Report for the Year 1891. London: Her Majesty's Stationery Office. Also Eyre and Spottiswoode, Fleet Street and Abingdon Street; J. Menzies and Co., Edinburgh and Glasgow; and Hodges, Figgis, and Co., Dublin.

THIS report may be considered satisfactory. The law concerning the manufacture and storage of explosives, if not perfect, certainly does not err in the direction of needless stringency, and the inspectors are evidently discharging their duties with great care and discretion. Fault can be found only with the local authorities, who are sometimes apt to impose penalties disproportionately small.

Only one death has occurred during the year from

accidents by fire or explosion during the process of manufacture. The total number of factories under continuing certificate and licence is 125, in addition to 123 so-called "toy firework" factories.

Twelve new explosives have been added to the authorised list; these, however, present no decidedly novel features. A great variety of smokeless or quasi-smokeless powders are now on the market.

Proceedings for irregularities in factories are now rare. In one case only was it necessary to put the law in force. The illegal manufacture of fireworks still occurs; one offender in Lambeth was only detected in consequence of an accident, and was fined £25 and costs.

The precautions necessary for the electric lighting of factories for explosives have required considerable attention. Illegal storage has rendered proceedings necessary in nine cases. A firm at Chesterfield were fined £4 for keeping detonators in an unauthorised place, so that they were stolen by a boy and distributed among his companions. The importance of keeping explosives out of the way of children and youths has been fully shown by the accidents which have happened in the course of the year. Not a few mishaps are due to the absurd custom of allowing miners, &c., to store in their houses the powder required in their daily work.

Many of the accidents occurring during the use and conveyance of explosives are due to conduct which was not merely grossly illegal, but, even more, decidedly irrational. Careless thawing of dynamite, blasting gelatin, &c., has given rise to no little mischief. In consequence, Nobel's Explosives Company have deemed it necessary to send round a special warning to their customers.

The number of outrages with explosives in Great Britain and Ireland, although not so great as in certain foreign parts, is enough to occasion a painful sense of uneasiness and justify the question whether the convenience of "high" explosives in engineering and military operations really compensates for the facilities they afford to the criminal classes.

The account of the tremendous explosion which took place at Rome on April 23, 1891, presents some very instructive features. The seismometers at the Alban Hills Observatory, at the distance of eighteen miles, showed three distinct earth waves, thus proving, as in the great Stowmarket case of 1871, that in severe explosions the shock is conveyed not merely in the air, but also through the ground. The explosion was ascribed to the spontaneous ignition of parachute or signal rockets. The committee of investigation denounced "mixed storage," which in this country is never sanctioned.

A very interesting explosion took place at the Schlebusch Dynamite Factory, near Cologne, on June 3. The magazine contained 1200 kilos. of nitroglycerin, was exploded by lightning in spite of the conductors which had been examined in May, and had been found in perfect order.

Some drunken men at Cheyenne placed a target against a magazine containing 1200 lbs. gunpowder, 600 lbs. dynamite, and a quantity of detonators. After a few shots they succeeded in blowing up the magazine and themselves.

Two samples of gun-cotton were examined which may lay claim to a historical character. One of these was taken in 1887 from the river passing the gun-cotton works at Stowmarket, having thus been under water since August 11, 1871. The other was dug up in February, 1891, on the site of the old exploded magazine of the same factory, and had been buried for 19½ years. Both samples were in perfect condition without any sign of deterioration. This not only proves the stability of well-made gun-cotton, but shows the good quality of the gun-cotton exploded on the memorable 11th of August, and that, as the chemists who gave evidence at the inquest

unanimously concluded, the mischief was occasioned by a portion of the gun-cotton having been maliciously tampered with.

The use of the electric light in magazines or factories does not necessarily exclude all danger. If a glow-lamp is broken in an atmosphere of gunpowder dust the carbon filament may for a moment retain heat enough to ignite the suspended dust. This was experimentally demonstrated at the Waltham Abbey Gunpowder Factory. There are the further risks from short-circuiting, heating of conductors, and sparking. The possible fall of a lamp from any cause must also be considered.

It is to be hoped that the action of the inspectors will gradually educate the public up to a higher grade of intelligence concerning the possession and the use of explosives. Even coroners, magistrates, &c., are at present sometimes in a perilous state of ignorance.

Elements of Physics. By C. E. FESSENDEN, Principal of the Collegiate Institute, Peterborough, Ontario. London and New York: Macmillan and Co., 1892, pp. 229.

THIS little work is by no means devoid of commendable features. The introductory chapter on matter and its properties is admirably written. We do not assert that the views advanced are novel, but they are put in a manner which must be fully intelligible to the young. We cannot help admiring the manner in which the attention of the pupil is called to facts which are always at hand, and from which the elementary truths of physics may be gathered. Thus he is quietly trained in the great arts of observing phenomena, and deriving from them the right conclusions,—the double process,—of which at the very least three-fourths of the business of our life consists. The term "phenomenon" is well explained, but explained as ably as it may be, the quacks have once for all got hold of it and will persist in its misuse as long as the English language is spoken.

As regards the scale of hardness of minerals the author has committed an error, clerical or typographical, in ascribing it to Mohr in place of Mohs. A careful student will be able to learn from this book not merely the elements of physics, but what is of even wider importance, the art of observation.

The Late Professor A. W. von Hofmann.—The interment of this illustrious *savant* took place on the 9th ult. Baron von Mirbach, on behalf of the Emperor and Empress, placed a splendid wreath upon the coffin. The Empress Frederick, the Grand Duchess of Baden, and the town of Giessen had also sent magnificent floral offerings. The Minister of Public Instruction was unable to be personally present, but was represented by Dr. Althoff. The University was represented by the Rector, Dr. Foerster, the Judge of the University Court, Daude, and the Dean, Prof. Diels. The Academy of Sciences was represented by the perpetual secretaries, Professors Auwers and Mommsen, the Imperial Physico-technical Institute by Privy Councillor von Helmholtz, the Patent Office by Privy Councillor Rommel, and the Imperial Sanitary Office by Dr. Koehler. The Technical High School and the Agricultural High School were represented by their Rectors. Numerous Universities and Chemical Societies had sent splendid garlands. The most distinguished representatives of the various Societies took part in the ceremonies. The eulogium was pronounced by P. Stechow. The students of the first chemical institute of the University opened the procession to the cemetery. Then followed the funeral car drawn by six horses, and the carriages with the mourners; whilst the great body of the students with numerous banners closed the procession.—*Chemiker Zeitung.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 20, May 16, 1892.

Contribution to the History of the Silico-carbon Compounds.—P. Schützenberger.—Some years ago, the author, in conjunction with M. Colson, described certain tertiary compounds consisting of carbon, silicon, and oxygen, or of carbon, silicon, and nitrogen. They are obtained by heating crystalline silicon to a red-white heat either in an atmosphere of carbonic acid or of carburetted gas and nitrogen. All these compounds are powders of a green colour, infusible, not attacked by hydrofluoric acid and by caustic alkalis even in concentrated solutions. They are attacked at nascent redness by melting potassa. In all, the carbon associated with silicon resists combustion at a red heat by means of free oxygen or of copper oxide. The carbon of these compounds can be burnt only on heating these compounds to redness along with basic lead chromate. The author has since obtained a new silicon carbide, SiC. This compound is a light green powder not attacked by boiling solution of potassa or by hydrofluoric acid, infusible and fixed.

Method for Separating the Xylenes.—J. M. Crafts.—For separating the xylenes, a weighed quantity of 10 to 20 grms. of the crude sample is added to 2½ parts of concentrated sulphuric acid in a tube of Bohemian glass. The length in millimetres occupied by the stratum of xylene is measured, and the tube is sealed and heated for an hour to 120°, shaking it vigorously. A saturated hydrocarbon remains on the surface as an insoluble stratum, but before measuring it is necessary to add 3 or 4 parts of a mixture of equal volumes of hydrochloric acid and of water, shaking, and allowing it to settle for an hour, so as to separate a portion which has been dissolved by the sulphonic acid. The tube must not be allowed to cool entirely to avoid a deposition of crystals. The hydrocarbon is measured and separated by means of a parting funnel; the acid solution is returned to the tube, which is sealed again and heated to 122° for twenty hours. By this treatment 97 per cent of the metaxylene are separated in a layer which is measured. The measurement is controlled by weighing after the metaxylene has been distilled with water to eliminate certain black substances; an operation which involves a loss of about 0.2 gm. The sulphones of the para- and ortho-xylenes and of ethylbenzene show only mere traces of decomposition at 122°. If heated more strongly they are decomposed without distinct fractionation, and it is advantageous to recover the whole by heating the solution after the removal of the metaxylene to 175° for twenty hours. The three recovered hydrocarbons are dissolved in three portions of sulphuric acid, and a volume of concentrated hydrochloric acid is added to the solution when cold. When the metaxylene has been separated, the sulphone of the paraxylene alone is precipitated in fine slender lamellæ, which are washed in concentrated hydrochloric acid upon an asbestos filter until the washings no longer give a reaction with barium chloride. The crystals are then exposed to the air until their weight is constant in order to find the proportion of paraxylene. The orthoxylene and ethylbenzene are finally separated by the process given by M. Friedel and the author in the "Dictionnaire de Wurtz" (Supplement, p. 1655).

Mechanical Determination of the Boiling Points of Compounds, with a Simple Terminal Substitution.—G. Hinrichs.—This paper is not adapted for useful abstraction.

Proximate Analysis of Chlorophyllic Extracts.
Nature of Chlorophyllone.—A. Etard.—The author's

procedure may be summarised as follows:—The green plants, dried at the ordinary temperature and coarsely powdered, are completely exhausted in the cold by means of carbon disulphide acting upon at least 4 kilos. of the dried material. After distilling off the solvent there remains an extract of a waxy consistence. Alcoholic extracts, if prepared directly, are so complex that their analysis may be regarded as impossible. **Sulphocarboinic Extracts.** *Group 1.*—The solid waxy extract if ground up with cold alcohol until this solvent runs off colourless, leaves a greenish mass, which on successive crystallisations, first from benzene, and then from acetic ether in presence of animal charcoal, always yields substances perfectly white and often well crystallised. These substances are solid carbides and high alcohols, glycols, and glycerines. *Group 2.*—The alcoholic mother-liquors are distilled *in vacuo*, the residue taken up in potassa at 2 per cent, and an excess of ether, contains alkaloids, alcohols, glycols, and chlorophylls. *Group 3.*—The preceding alkaline solution if acidulated in presence of ether yield to the latter saturated fatty acids. **Alcoholic Extracts.** *Group 4.*—The alcoholic extract (from material previously exhausted with carbon disulphide) prepared in heat and then solidified by concentration, is exhausted by grinding up with cold alcohol in presence of its own volume at least of ground glass. There remains a solid residue which is titrated with ether. *Group 4*, which the ether leaves as a residue, contains extractive matters free from chlorophyll, of an astringent taste, and generally of a brown colour. *Group 5.*—The ethereal extract from the foregoing process yields on evaporation chlorophylls capable of separation and purification. *Group 6.*—The alcoholic solutions from *Group 4* distilled *in vacuo* leave a residue from which cold ether extracts a large quantity of very green chlorophyll. *Group 7.*—The residue insoluble in ether derived from the foregoing group contains extractive matters nearly colourless, soluble in water and alcohol, and mostly nitrogenous. The hypochlorine of Pringsheim is probably, according to Tchirsch, identical with the chlorophyllane of Hoppe-Seyler. It is very doubtful whether it is a definite chemical individual.

Influence of the Nature of the Soil upon Vegetation.—J. Raulin.—In experiments with potatoes the author found the crop decrease in proportion as the clay and limestone in the soil were augmented, but increased with increasing proportions of sand and humus.

Zeitschrift für Anorganische Chemie.
Vol. i., Part 3.

Research on the Atomic Weight of Copper.—Th. Richards.—Second communication. In part already inserted. (See CHEMICAL NEWS, vol. lxx., p. 236).

New Method for the Titration of Ferric Salts.—Hermann Morah. The volumetric method here proposed depends on the two best known reactions of ferric oxide, *i.e.*, on the formation of prussian blue from a ferric salt and potassium ferrocyanide, and the production of red iron sulphocyanide by means of potassium sulphocyanide. The solution of a ferric salt gives with ferrocyanide a precipitate of prussian blue, until all the ferric oxide present has been thrown down. Even a solution of iron sulphocyanide is precipitated and decolourised by potassium ferrocyanide. If a solution which, in addition to suspended prussian blue, still contains traces of a ferric salt, is mixed with potassium sulphocyanide as an indicator, the red colour of iron sulphocyanide appears. But on the further addition of potassium ferrocyanide this colour must disappear with a further formation of prussian blue at the moment when all the existing iron has been transformed into this compound. It was above all things necessary to assume that prussian blue is a chemical individual of the constant composition $\text{Fe}_4(\text{FeCy})_6$, as it has been proved by A. Classen (Mohr's "Titrimethode," sixth edition, 1886, p. 235). A second necessity is to render the end of the precipitation and the disappearance

of the red colour distinctly visible. This is easily effected, as prussian blue is quite insoluble in ether, which readily dissolves iron sulphocyanide. The latter compound can be withdrawn from very dilute aqueous solutions by shaking out with ether. In carrying out the titration of ferric salts on the above principle the reaction between the ferric salt and the ferrocyanide must be effected in bottles with well-fitting ground stoppers, shaking violently. The opening of the bottles must be performed very cautiously so as to minimise the evaporation of ether. In order to obtain very exact results it is recommended to effect two titrations, the first as a preliminary and the second as final. The ferric solution in question, or an aliquot portion, is mixed in a $\frac{1}{2}$ -litre stoppered bottle with a little potassium sulphocyanide and about 50 c.c. of ether, so as to take at once a deep red colour. Solution of potassium ferrocyanide of known strength is then gradually added from a burette, shaking the bottle violently each time until after settling the supernatant stratum of ether appears of a faint rose or colourless. After this preliminary experiment the ferric solution, or an aliquot portion of it, is put in a $\frac{1}{2}$ -litre stoppered bottle, mixed with nearly the number of c.c. of ferrocyanide solution which were used in the preliminary experiment, stirred up, and the potassium sulphocyanide and a sufficient quantity of ether are then added. After shaking and allowing the two liquids to separate, the ether appears only of a very faint rose-colour, and one or a few drops of the ferrocyanide suffice to decolourise it completely. The colourless character of the supernatant ether may best be recognised on viewing it obliquely from below. The standard of the ferrocyanide may be found by dissolving weighed quantities of pure iron in hydrochloric acid with the addition of a little potassium chlorate, expelling all the excess of chlorine by ebullition and determining the number of c.c. of the solution of ferrocyanide which are necessary to convert the ferric salt present into prussian blue. We thus obtain directly the quantity of iron corresponding to 1 c.c. of the standard solution. No ferrous salt must be present along with the ferric compound.

Contributions to a Knowledge of the Compounds of Palladium.—Michael Frankel.—This important memoir will, if possible, be inserted in full.

Possibility of a Gaseous State of Certain Metals at Temperatures below their Melting-Point.—W. Spring.—We notice the following experiment:—Leaflets of silver, platinum, and gold, were heated to 150° with concentrated hydrochloric acid in sealed tubes. The metals were dissolved and the chlorides formed were reduced by the hydrogen evolved from the metals and the hydrochloric acid. They were deposited on the sides of the tubes in microscopic crystals. It may be assumed that in this experiment even the platinum existed for some time as a liquid before taking a crystalline form.

The Direct Quantitative Separation of Chlorine, Bromine, and Iodine.—P. Jannasch and K. Aschoff.—Certain inaccuracies which the authors encountered in their earliest experiments are traced to the use of an impure acetic acid.

Quantitative Separation of Iodine and Chlorine by direct Precipitation with Solution of Thallium Sulphate.—P. Jannasch and K. Aschoff.—Hübner, Spezia, and Ferichs have some time ago made known a method for the determination (partly gravimetric and partly volumetric), of iodine in presence of chlorine or bromine, depending on the sparing solubility and the yellow colour of thallos iodide. The method proposed by the authors for separating I and Cl by means of thallium sulphate is purely gravimetric, and depends on the absolute insolubility of thallos iodide in cold water containing alcohol even in presence of ammonium salts and other compounds in which thallium chloride remains in solution. A separation of bromine and chlorine in the above manner seems not possible, since thallos bromide is in all cases too soluble.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

The Actinograph.—We have pleasure in informing you that Messrs. Hurter and Driffield have finished their calculations of Light Scales of other latitudes for their actinograph, and shortly the instrument will be ready for delivery as per list which follows. Thus it can be supplied for use in any part of the world.— 0° Equator. North: 20° , 30° , 40° , $47^{\circ} 30'$, $52^{\circ} 30'$, $57^{\circ} 30'$, $62^{\circ} 30'$. South: 10° , 20° , 30° , 40° , $47^{\circ} 30'$.—MARION AND CO.

MEETINGS FOR THE WEEK.

- TUESDAY, 7th.—Photographic, 8.
Royal Institution, 3. "Some Aspects of Greek Poetry," by Prof. R. C. Jebb.
WEDNESDAY, 8th.—Geological, 8.
THURSDAY, 9th.—Royal Institution, 3. "On Faust," by R. G. Moulton, M.A.
Mathematical, 8.
FRIDAY, 10th.—Royal Institution, 9. "Magnetic Properties of Liquid Oxygen," by Prof. Dewar, F.R.S.
Astronomical, 8.
Physical, 5. "Some Points connected with the Electromotive Force of Secondary Batteries," by Dr. J. H. Gladstone and Mr. Hibbert. "Workshop, Ballistic, and other Shielded Galvanometers," by Prof. W. E. Ayrton and Mr. Mather.
SATURDAY, 11th.—Royal Institution, 3. "Some Modern Discoveries in Agricultural and Forest Botany," by Prof. H. Marshall Ward, F.R.S.

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Nature; complete set 1869 to 1888; 39 vols. cloth, £8 8s.
Chemical News, COMPLETE SET, 1860 to 1889; 60 vols. cl., £20.
Chemistry applied to Arts and Manufactures by writers of eminence (Schorlemmer and others); engravings, 8 vols. (1880), £4, for 45s.
Gmelin's Handbook of Chemistry (Organic and Inorganic), by H. V. WATTS, complete set, 19 vols. cl., scarce, £20, for £7 17s. 6d.
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THE CHEMICAL NEWS.

VOL. LXV., No. 1698.

RESOLUTIONS ADOPTED BY THE INTERNATIONAL COMMISSION FOR THE REFORM OF CHEMICAL NOMENCLATURE ASSEMBLED AT GENEVA FROM THE 19TH TO THE 22ND APRIL, 1892.

1. THAT in addition to the usual name, each organic compound shall have an official name assigned to it, enabling it to be found under a distinct heading in tables and dictionaries. The Commission expresses the wish that authors would adopt the habit of mentioning in their memoirs the official name in parenthesis along with the name which they have selected.

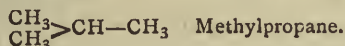
2. That for the present only the nomenclature of compounds of known constitution be considered, the question of bodies of unknown constitution being postponed.

I.—Hydrocarbons.

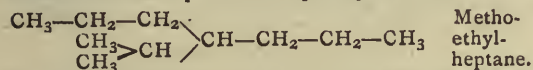
3. The termination *ane* is to be adopted for all the saturated hydrocarbons.

4. The present names of the four first normal saturated hydrocarbons (*methane, ethane, propane, butane*) are to be retained; names taken from Greek numerals to be used for those which contain more than four atoms of carbon.

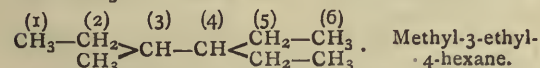
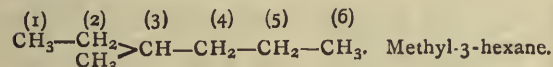
5. Hydrocarbons with arborescent chains are to be regarded as derivatives of the normal hydrocarbons, and their name is referred to the longest normal chain which can be established in their formula, adding the designation of the lateral chains.



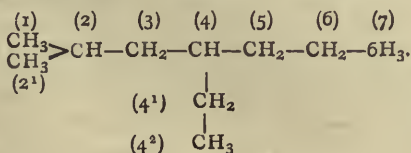
6. When a hydrocarbon radicle is introduced into a lateral chain, metho-, etho-, &c., is to be used in place of methyl-, ethyl-, &c., prefixes reserved for cases where substitution takes place in the principal chain.



7. The position of the lateral chains is to be indicated by figures indicating to which of the carbon atoms of the principal chain they are attached. The numbering is to commence from that end of the principal which is nearest to a lateral chain. In case the two lateral chains nearest to the extremities are placed symmetrically the preference is to be given to the simplest.



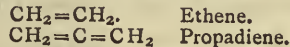
8. The atoms of carbon of a lateral chain are to be designated by the same figure as the atom of carbon to which the chain is attached, with the addition of an index fixing their rank in the lateral chain, setting out from the point of attachment.



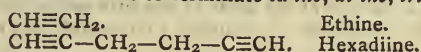
9. In case of two lateral chains attached to the same atom of carbon, the order in which these chains are announced is to correspond to their order of complication, and the simplest indices are to be accented.

10. The same method of numbering is to be adopted for lateral chains connected to closed chains.

11. In non-saturated hydrocarbons with an open chain possessing a single double connection, for the termination *ene* of the corresponding saturated hydrocarbon the termination *ene* is to be substituted; if there are two double connections the name is to end in *diene*, if three in *triene*, &c.

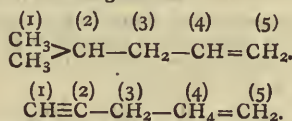


12. In like manner the names of hydrocarbons with triple connection are to terminate in *ine*, *di-ine*, *tri-ine*.

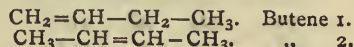


13. If there are simultaneously double and triple connections, the terminations *enine*, *dienine*, &c., are to be used.

14. The non-saturated hydrocarbons are to be numbered like the corresponding saturated hydrocarbons. In case of ambiguity or of the absence of a lateral chain, the number 1 is to be attached to the terminal carbon nearest the connection of the highest order.



15. If necessary, the place of the double or triple connection is to be indicated by the number of the first carbon atom to which it is attached.



16. The saturated hydrocarbons with closed chains are to take the names of the corresponding saturated hydrocarbons of the fatty series, preceded by the prefix *cyclo* (cyclohexane for hexamethylene).

17. The numbering of the hydrocarbons is to be preserved in all their substitution products.

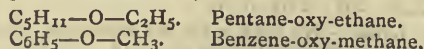
II.—Functions.

18. *Alcohols* and the *phenols* are to be designated by the name of the hydrocarbon from which they are derived, followed by the suffix *ol* (methanol, pentenol).

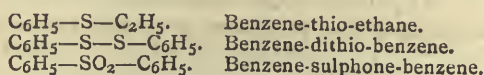
19. In the case of polyhydric alcohols or phenols, between the name of the fundamental hydrocarbon and the suffix *one* of the particles *di*, *tri*, *tetra*, indicating hydricity, is to be interposed (propanetriol for glycerin, hexanehexol for mannite).

20. The name mercaptan is abandoned, and this function is to be expressed by the suffix *thiol* (ethane-thiol).

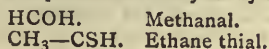
21. The oxy ethers are to be designated by the names of the component hydrocarbons, connected by the particle *oxy* (a provisional decision).



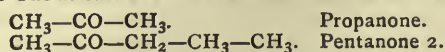
22. The sulphides are to be designated by the syllable *thio*, the disulphides by *dithio*, the sulphones by *sulphone* (a provisional decision).



23. The *aldehydes* are to be characterised by the suffix *al* added to the name of the hydrocarbon whence they are derived, and the sulphuretted aldehydes by the suffix *thial*.



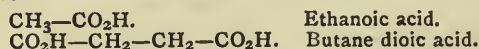
24. The *ketones* are to receive the termination *one*.



The diketones, triketones, thioketones, are to be designated by the suffixes *dione*, *trione*, *thione*.

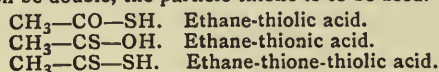
25. The present nomenclature of the *quinones* is to be retained.

26. The name of the monobasic acids of the fatty series is to be taken from that of the corresponding hydrocarbon followed by the suffix *oic*. The polybasic acids are to be designated by the terminations *dioic*, *trioic*, *tetroic*.

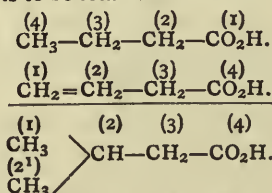


27. In the case of the acids of the fatty series, carboxyl is to be considered as forming an integral part of the carbon chain.

28. The acids in which one or two atoms of sulphur displace as many atoms of oxygen of the carboxyl are to be named as follows:—The sulphur simply combined with the atom of carbon is to be denoted by *thiol*; if the connection be double, the particle *thione* is to be used.



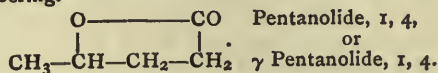
29. In monobasic acids containing a normal or symmetric chain, the carbon of the carboxyl is to be numbered 1. In other cases the numbering of the corresponding hydrocarbons is to be retained.



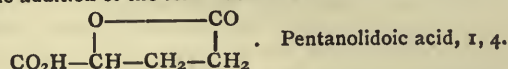
30. The present names for the salts and the compound ethers are to be retained.

31. The anhydrides are to retain, as at present, names derived from those of the corresponding acids (ethanoic anhydride).

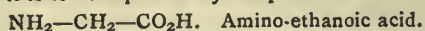
32. The *lactones* are to be designated by the suffix *olide*. The position in the principal chain occupied by the alcoholic oxygen with reference to the carbonyl may be expressed by the Greek letters α , β , γ , δ , and the customary numbering.



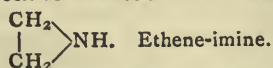
The *lactonic acids* derived from bibasic acids are to be named like the *lactones* from which they are derived, with the addition of the termination *oic*.



33. *Amines*.—No change for the compound ammonias (ethylamine, ethylmethylaniline, and ethene-diamine). When the group NH_2 is considered as a substituting group it is to be expressed by the prefix *amino*.



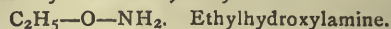
Substances in which the bivalent group NH closes a chain composed of positive radicles are to be called *imines*:—



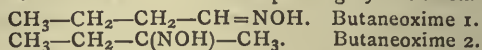
The Commission proposes to name the group NH_2 *amigenes*, and the group NH *imigenes*.

34. The nomenclature in use for the phosphines, arsines, stibines, sulphines is to be retained.

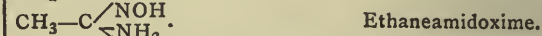
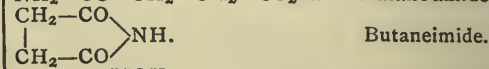
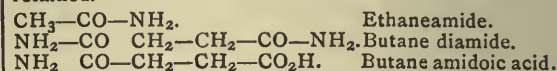
35. The derivatives of *hydroxylamine* formed by displacement of the hydrogen of the hydroxyl are to be designated by the suffix *hydroxylamine*.



The oximes are to be denominated by adding the suffix *oxime* to the name of the corresponding hydrocarbon.

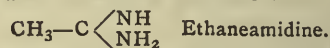


36. The names of *amides*, *imides*, *amidoximes* are to be retained.



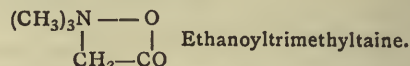
37. The generic term *urea* is to be retained. It is to be employed as a suffix for the alcoholic derivatives of urea, whilst the acid substitution derivatives are to be known as *ureides*. Substances derived from two molecules of urea are to be designated by the suffixes *diurea*, *diureide*. The acid ureides are to take the name of ureic acids. The terminations *uramic* and *uric* are to be rejected.

38. *Amidines*.—This suffix is retained.

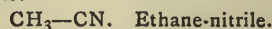


39. The generic term *guanidine* is to be retained, but different guanidines are to be named as substituted derivatives of diamido-carbo-imidine.

40. *Betaine*. Suffix *taine*.

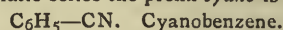


41. *Nitriles*.—In the case of the derivatives of the fatty series, where the group CN forms part of the principal chain, the name of the hydrocarbon is to be followed by the suffix *nitrile*.



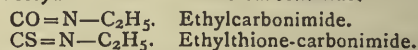
The question is left undecided in cases where this group forms part of a lateral chain.

In the aromatic series the prefix *cyano* is to be adopted.



42. *Carbonylamines*.—The present nomenclature is to be retained.

43. *Isocyanic Ethers*.—Suffix *carbonimide*.

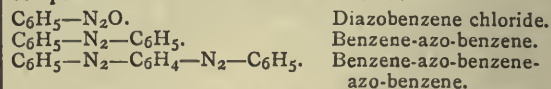


44. *Cyanates*.—This name is reserved for the two ethers which on saponification yield cyanic acid or its products of hydration.

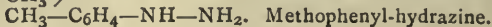
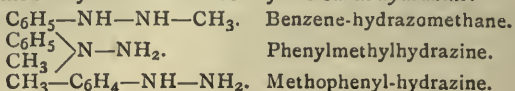
The name *thiocyanate* is to be substituted for *sulphocyanate*.

45. *Nitro-derivatives*.—The present nomenclature is not to be changed.

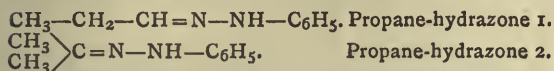
46. *Azo-derivatives*.—The denominations *azo*, *diazo*, *hydrazo*, *azoxy* are to be retained, but the names of these compounds are to be modified as follows:—



47. The symmetrical *hydrazines* are to be considered as hydrazo-derivatives and named as such. The asymmetrical hydrazines are to be designated by the names of radicles which they contain followed by the suffix *hydrazine*.



48. The name of the hydrazones is formed by replacing the termination *al* or *one* of the aldehydes and the ketones by the suffix *hydrazone*.

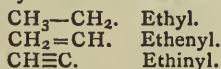


The term *dihydrazone* is to be substituted for osazone.

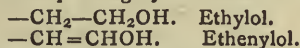
49. The full discussion of the nomenclature of substances exhibiting complex functions was adjourned, and the study of this question remitted to the International Commission, so that it may prepare a project on this point which may be submitted to the next Congress. The Commission should endeavour to reconcile the demands of spoken nomenclature with those of a terminology suitable for dictionaries.

III.—Radicles.

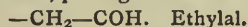
50. The names of monovalent radicles derived from hydrocarbons by the elimination of an atom of hydrogen are to terminate in *yl*. This termination is to be substituted for the termination *ane* in the case of the radicles of the saturated hydrocarbons; it is to be added to the complete name of the hydrocarbon if this is not saturated.



51. The radicles of alcoholic function, *i.e.*, those derived from alcohols by eliminating an atom of hydrogen united directly to carbon, are to be named by adding *ol* to the radicle of the corresponding hydrocarbon.



52. The radicles of the aldehydes are to be named like those of the alcohols, putting *al* instead of *ol*.



53. The radicles of the acids which have retained the acid function, *i.e.*, which are derived from the corresponding acid by the elimination of an atom of hydrogen linked to the carbon, are to be named similarly, substituting *oic* for *al*.



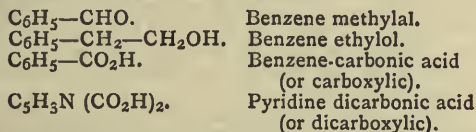
Those, on the contrary, which are derived from an acid by removal of a carboxylic hydroxyl are to be named by transforming the termination *oic* into *oyl*.



54. When two radicles are united to the same atom, the more complicated of them is mentioned first (phenyl-methylhydrazine, pentylmethylamine).

IV. Aromatic Series.

55. In the case of aromatic derivatives, and in all substances containing a closed chain, all the lateral chains are considered as substitution groups.

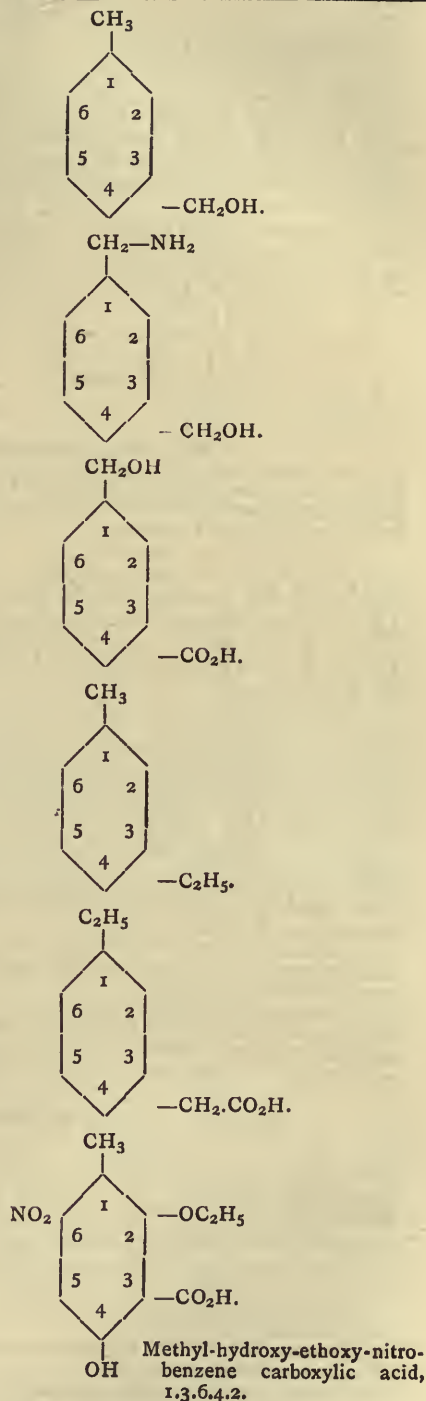


(The exigencies of language will decide which of these two last expressions is preferable).

56. The carbon atoms of the benzene nucleus and the lateral chains attached to it are to be numbered from 1 to 6.

57. In a poly-substituted derivative of benzene the index 1 is to be assigned to the substituting group in which the atom linked directly to the nucleus has the lowest atomic weight.

58. The place 1 being thus fixed, the indices of the groups are to be announced in the order of the increasing weights of the atoms directly linked to the nucleus. If



the soap should be dissolved by adding 100 c.c. of recently boiled distilled water, and warmed on the steam-bath with occasional shaking until the soap is completely dissolved.

Setting Free the Fatty Acids.—When the soap solution has cooled to about 60° or 70° C., the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid solution mentioned above.



FIG. 3.

Melting the Fatty Acid Emulsion.—The flasks should now be re-stoppered as in the first instance, and the fatty acid emulsion melted by replacing the flasks on the steam bath. According to the nature of the fat examined the time required for the fusion of the fatty acid emulsions may vary from a few minutes to hours.

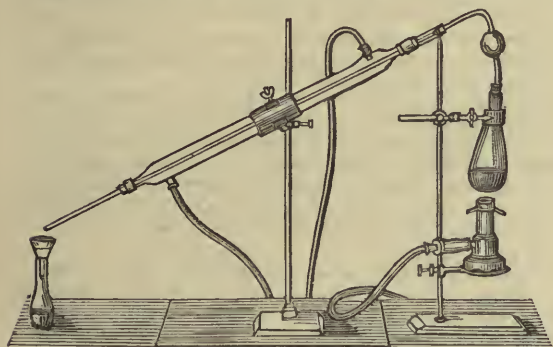


FIG. 4.

The Distillation.—After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flasks are cooled to room temperature and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at white heat, into distilled water, and keeping it under water until used. The flask is now connected with a condenser (Fig. 4), slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way

as to collect 110 c.c. of the distillate in as nearly as possible thirty minutes. The distillate should be received in flasks accurately graduated at 110 c.c.

Titration of the Volatile Acid.—The 110 c.c. of distillate, after thorough mixing, are filtered through perfectly dry filter paper and collected in a flask graduated at 100 c.c. The 100 c.c. of the filtered distillate are poured into a beaker holding from 200—250 c.c., 0.5 c.m. phenolphthalein solution added, and decinormal barium hydrate run in until a red colour is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red colour produced remains apparently unchanged for two or three minutes.

(To be continued.)

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 268).

Third Series.

It is only by gradual approach that very accurate quantitative work may be realised, and the earlier series were absolutely necessary as a training and preparation for the present one. This series had for its object not only an investigation of the effect of increased refinement, but also a definite proof that the amount of acid present in cupric sulphate was unaffected by the operations involved in the dehydration of the salt. To this end the first sample was not dehydrated at all, the second was heated only to 250°, and the third was exposed to the full heat of 365°, after the addition of sulphuric acid. Since the percentage of acid found in these samples did not vary beyond a reasonable limit of error, the proof is satisfactory.

The additional precautions taken in the preparation of the materials have already been mentioned under appropriate heads. Besides these, many refinements of manipulation were employed, too numerous to be fully described. For example, phosphorous pentoxide was used as a drying agent in the desiccator, and immediately after the introduction of a hot crucible the air was exhausted with a good air pump and re-admitted through a series of drying tubes. This method, of course, absolutely prevents the absorption of moisture by the contents of the crucible while cooling.

Again, in the ninth experiment, the solution of the perfectly neutral sodic sulphate was transferred to a small flask, heated to 103°, and evaporated by means of a current of pure dry air. When dry, the sulphate was gently ignited and weighed in the flask, and subsequently fused in a platinum crucible. The flask lost 0.00010 grm. during the operations, and the sodic sulphate lost 0.0003 grm. upon fusion. With the exception of the small flask, all the apparatus was of platinum. The sodic sulphate formed in the second experiment, and the sodic carbonate required in the third, were not determined.

The last experiment of the series was not of the same grade of refinement with the others. It is only included here because the same preparation of cupric sulphate was used in its execution.

The determination of the sulphuric acid by still another method was the object of this experiment. Baric sulphate was precipitated from a boiling solution of cupric sulphate strongly acidified with hydrochloric acid. After weighing as usual, the perfectly white precipitate was fused with

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

Analysis of Cupric Sulphate.—Third Series: Data.

(Weights reduced to vacuum standard).

No. of Experiment.	CuSO ₄ ·5H ₂ O taken. Grms.	CuSO ₄ found. Grms.	Metallic Cu found. Grms.	Na ₂ CO ₃ found by methyl orange. Grms.	Na ₂ CO ₃ found by phenolphthalein. Grms.	Sodic sulphate found. Grms.
7.	2'88307	—	0'73380	1'2242	1'22435	1'63994
8.	3'62913	at 260° 2'32373	0'92344	1'5407	1'54080	—
9.	5'81352	at 370°± 3'71680	1'47926	—	—	3'30658
	CuSO ₄ ·5H ₂ O taken.		Baric sulphate found (uncor.).	Argentich chloride found.	Baric chloride calculated.	Baric sulphate corrected.
10.	3'1902		2'9967	0'0284	0'0206	2'9761

pure sodic carbonate, and the resulting cake thoroughly lixiviated with boiling water and dilute sodic carbonate solution. In the filtrate, the chlorine, which had been originally present as baric chloride occluded in the sulphate, was determined in the usual manner. Traces of baric sulphate and argentic chloride must have been dissolved in the wash water, but these errors tend to counterbalance one another, and hence no correction was made for them. Finally, the weight of baric chloride, calculated from the amount of chlorine found, was subtracted from the weight of baric sulphate; and from the corrected weight thus obtained the percentage of sulphuric acid in cupric sulphate was calculated. The astounding agreement of this experiment with the others may be nothing more than accident. In any case, the uncertainty of the atomic weight of barium, and the very unsatisfactory nature of baric sulphate, combine to make a repetition of the experiment of little value for the present purpose; but the method seems to be of value, and will form a subject of future investigation in this laboratory. It is well known that baric sulphate has great power of occluding many salts, but few experimenters seem to have realised that the occlusion of most metallic sulphates tends to decrease the amount of precipitate obtained. This fact was recognised by Professor Jannasch and the writer (*Four. für Prakt. Chemie*, xxxix., 321) in 1889, and would influence the controversy between Ostwald (*Lehrbuch der Allgem. Chem.*, i., 53) and Krüss (*Annalen*, cclxii., 40). The occlusion of baric chloride of course increases the amount of precipitate when sulphuric acid is to be determined, and diminishes it when barium is to be determined. With care this last error may be reduced to a very small amount, but it is doubtful if it has ever been wholly avoided. A trace only of copper was found in the precipitate obtained in the experiment described above, showing that cupric chloride is not occluded to any essential extent.

In spite of the fact that the important analyses of the third series were far more carefully performed than those of the second, the result was no more satisfactory than before. It was therefore apparent that a point had been reached beyond which further refinement was unavailing, and that the reason of the discrepancy must be sought, not in accidental or variable impurity, but rather in some property inherent in the purest cupric sulphate,

Third Series: Results.

No. of Expt.	Water lost at 260°.	Water lost at 370°±.	Copper found.	SO ₄ found from Na ₂ CO ₃ (average).	SO ₄ found from Na ₂ SO ₄ .
7.	—	—	25'452	38'443	38'433
8.	35'970	—	25'446	38'435	—
9.	—	36'067	25'445	—	38'431
				From baric sulphate.	
10.					38'434
Average	35'970	36'067	25'448	38'439	38'433

Percentage Composition of Cupric Sulphate.

	Second Series.	Third Series.	Theoretical.	
			Cu = 63'60.	Cu = 63'33.
Water . . .	36'068	36'067	36'0695	36'109
Copper . . .	25'450	25'448	25'4665	25'385
SO ₄ . . .	38'436	38'436	38'464	38'506
	99'954	99'951	100'000	100'000

(To be continued.)

A METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. BROWNING.

(Concluded from p. 272).

THE next experiments were directed toward a separation of strontium and calcium nitrates. Definite amounts of a solution of strontium nitrate were measured from burettes into counterpoised beakers and weighed, as already described; the calcium nitrate was then added in solution, and the weight taken again. The water was evaporated, and the dry salts dissolved again in the least possible amount of water, and boiled with amyl alcohol (30 c.m.*) as before. The strontium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried, and weighed as previously described. The calcium was determined in the form of the sulphate by evaporation of the alcohol, treatment with an excess of sulphuric acid, and ignition.

Correction was made for the solubility of the strontium nitrate, and its consequent presence with the calcium, by calculating the amount dissolved in the portion of amyl alcohol employed to the condition of sulphate, and subtracting that quantity from the apparent amount of calcium sulphate found. The results of this mode of proceeding are recorded in experiments 10 and 11.

	SrO taken. Grm.	SrO found (corrected). Grm.	Error.	CaO taken. Grm.	CaO found (corrected). Grm.	Error.
10.	0'0911	0'0932	0'0021 +	0'0932	0'0907	0'0025 -
11.	0'0915	0'0945	0'0030 +	0'0933	0'0899	0'0034 -

After making the correction in the manner specified, it is evident that the amount of strontium indicated is greater than that originally taken. It is apparent, therefore, that the strontium nitrate must have been contaminated, probably mechanically, by the calcium salt, as the calcium salt is found to be correspondingly deficient in amount. It was thought best, therefore, to have recourse to a double treatment with the alcohol. Accordingly, after the first boiling already described, the alcohol

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, xlii., January, 1892.

carrying the greater part of the calcium in solution was decanted upon an asbestos felt under the conditions previously described, and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water, treated with a drop of nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water, 30 c.m.* of the alcohol were added, and the boiling repeated. The residue was filtered off upon the same felt through which the first portion had been decanted, and washed with amyl alcohol, care being taken to remove all particles of the residue from the beaker by careful rubbing. The crucible and residue were heated in an air-bath at 150° C. as before, and then weighed. The filtrate from the two treatments and the washings were treated differently in two series of experiments. In Series II. the filtrate was precipitated with sulphuric acid, ethyl alcohol being added to secure thorough mixture. The precipitated sulphate was filtered off upon asbestos, heated to low redness, and weighed. In Series III. the alcoholic filtrate was evaporated to a small volume, transferred to a weighed platinum crucible, and evaporated. The residue was ignited to burn off organic matter, treated with sulphuric acid, and again ignited at low redness and weighed.

Series II.

SrO taken.	SrO found (corrected).	Error.	CaO taken.	CaO found (corrected).	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
12. 0.1235	0.1239	0.0004 +	0.1290	0.1271	0.0019 -
13. 0.1237	0.1228	0.0009 -	0.1246	0.1226	0.0020 -
14. 0.1239	0.1239	0.0000	0.1248	0.1223	0.0025 -
15. 0.1974	0.1972	0.0002 -	0.0502	0.0492	0.0010 -
16. 0.1979	0.1978	0.0001 -	0.0496	0.0482	0.0014 -

Series III.

17. 0.0148	0.0155	0.0007 +	0.0256	0.0254	0.0002 -
18. 0.0183	0.0183	0.0000	0.1030	0.1015	0.0015 -
19. 0.0364	0.0366	0.0002 +	0.0516	0.0511	0.0005 -
20. 0.0365	0.0365	0.0000	0.0515	0.0513	0.0002 -
21. 0.0493	0.0494	0.0001 +	0.0515	0.0502	0.0013 -
22. 0.0497	0.0497	0.0000	0.0519	0.0511	0.0008 -
23. 0.0497	0.0503	0.0006 +	0.0249	0.0245	0.0004 -
24. 0.0729	0.0732	0.0003 +	0.0257	0.0251	0.0006 -
25. 0.0730	0.0732	0.0002 +	0.0255	0.0255	0.0000
26. 0.0744	0.0744	0.0000	0.0258	0.0260	0.0002 +
27. 0.0912	0.0910	0.0002 -	0.1286	0.1276	0.0010 -

The average error in the determination of strontium in both series is less than 0.0001 gm. + on the oxide; that of the calcium amounts to 0.0017 gm. - on the oxide in Series II., and to 0.0005 gm. - in Series III.

In both processes the correction for the solubility of strontium nitrate in amyl alcohol, determined as previously described, was applied—0.0020 gm. being added to the weight of the strontium oxide found after the double treatment with amyl alcohol, and 0.0035 gm. being deducted from the apparent weight of the calcium sulphate found before calculating it to the form of the oxide. The latter of the two processes, which are identical so far as handling of the strontium is concerned, yields the better results in the determination of the calcium, doubtless because a trifling amount of calcium sulphate remains in solution in the final filtrate in the former process, while in the latter every trace should be recovered. The deposition of minute traces of calcium in the precipitation of the strontium nitrate, to which reference has been previously made, is evidently a matter of no significance in comparison with the ordinary errors of manipulation.

Action of the Ethers of the Non-Saturated Acids upon Sodic Cyanacetic Ethers.—P. Th. Muller.—The author has examined the action of fumaric and citraconic ethers.—*Comptes Rendus*, cxiv, No. 21.

DETECTION OF THE HIGHER ALCOHOLS IN ETHYLIC ALCOHOL.

By M. C. BARDY.

THE author's method of operation is as follows:—Before all treatment we ascertain if the sample is rich in the higher alcohols or not. To this end we place in a tube 10 c.c. of the alcohol under examination with 100 c.c. of a standard solution of sodium chloride, agitate, and allow it to settle. Two cases may occur:—(a) the salt water retains the whole of the original liquid in solution; (b) an oily layer collects at the upper part of the tube. The course of procedure is the same in both cases, only the quantity of alcohol upon which we have to operate varies.

a.—The Brine does not Separate an Oily Liquid.

Take 100 c.c. of alcohol, introduce them into a large glass flask with a ground glass stopper at its upper part, and having a glass cock at its lower part, add 450 c.c. of a saturated solution of salt and then a quantity of pure water sufficient to re-dissolve the sodium chloride which is deposited (about 50 c.c.), introduce 60 to 70 c.c. of pure carbon disulphide, and shake briskly. Allow to settle for a few minutes and decant the sulphide into a flask like the former, but smaller (about 300 c.c.). Pour upon the milky liquid remaining in the large flask a further quantity of sulphide equal to the former. Shake up, decant, and repeat the treatment a third time, collecting in the smaller flask all the sulphides resulting from the exhaustion. If this treatment has been properly carried out the whole of the butylic and amylic alcohols will have been extracted by the sulphide.

To separate these alcohols add a quantity of concentrated sulphuric acid (about 2 c.c.), so that the yellow stratum formed by this acid may be more dense than the sulphide, and may easily reach the bottom of the flask. Agitate the mixture strongly, and then allow the acid to separate, assisting, if needful, the collection of the drops by giving the flask some shocks or some rotatory movements. Decant the acid into a small flask holding about 125 c.c. Repeat the acid treatment two or three times, using each time 1 c.c. of concentrated acid. Add these washing acids to the first acid collected, then heat the flask to 50° or 60° whilst passing a slight current of air over the surface of the liquid until all odour of carbon disulphide has disappeared. Add then a volume of glacial acetic acid almost equal to the volume of the sulphuric acid, and adapt to the neck of the flask a straight tube of one metre to serve as a refrigerant. Then heat the flask in a water-bath to about 100° for a quarter of an hour. When the etherification is complete remove the flask from the water-bath, and add to its contents 100 c.c. of brine. If the alcohol in question contains higher alcohols we see formed upon the surface of the liquid an oily layer of acetic ethers more or less abundant. To appreciate the volume of these ethers introduce the entire liquid into a flask of about 150 c.c. capacity, terminating at its lower part in a tube graduated in tenths of a c.c. and fitted with a cock.

Allow the oily layer to collect, decant the aqueous liquid by means of the cock in such a manner as to collect the ethers in the graduated part of the apparatus, plunge it into water at +15, and when an equilibrium of temperature has been obtained read off the volume of the oily stratum. The number read, multiplied by 0.8, gives the percentage of the butylic and amylic alcohols contained in the alcohol under examination.

b.—The Salt Water Separates an Oily Liquid.

As the alcohol in question contains in this case a large proportion of the higher alcohols, it is well to take only 25 c.c. as a sample and to add only 100 c.c. of brine and from 8 to 10 c.c. of pure water. The quantity of carbon disulphide does not need to be reduced, and the rest of the operation is effected as described in (a).

The carbon disulphide removes from the ethylic alcohol nothing except butylic and amylic alcohols; therefore, if the mixture contains propylic alcohol (normal or iso), this alcohol must be sought for in the liquid, which has been exhausted with carbon disulphide.

To this end the salty alcoholic liquid is distilled after having been first carefully filtered over moistened paper, and the product of the distillation is collected in a vessel containing an alcoholometer until this indicates 50°. At this moment the totality of the alcohol or of the alcohols has passed over. To find the proportion of propylic alcohol in this liquid two methods may be used. One of them, empirical, but generally sufficient, is the permanganate process of Barbet. The other, very accurate, is founded on Gossart's new process of homoetropy.—*Comptes Rendus*, cxiv., 1201.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.

Report to the Governors, April, 1892.

THIS report, which is presented by the council, must, we think, convince all who read it carefully that the Institute is not, as some persons are pleased to insinuate, a mere plaything for certain eminent persons, but that it has a very serious, well-defined object. For that object it is working earnestly and by no means unsuccessfully.

No inconsiderable number of young men who have studied at the various courses of the Institute are now filling honourable and useful appointments. Since 1887-8 the number of day students down to the winter term of 1891 has increased from 285 to 370. The students' fees last year were £4086 rs., as against £3772 6s. in 1890. Ten of the City Companies have come forward as benefactors to the Institute. The total income of the Institute for the year 1891 was £30,940 10s. 4d. Perhaps the least satisfactory of the Institute is the relatively small proportion of the chemical students. Thus, in the session ending in July, 1891, the day classes were attended only by 38 students out of a total of 185. In the evening classes there were 1240 students, of whom 99 only entered in the chemical department, the other departments having respectively 244 students (mechanical), 617 (electrical), 120 (applied art), and 160 (trade classes). This will be felt the more discouraging if we reflect that in the chemical arts we have comparatively the greatest difficulty in competing with our rivals.

It may be that the chemical arts and manufactures offer less remunerative positions than do the mechanical and especially the electrical trades. We should with all deference suggest that the Council of the Institute should make a careful investigation of the points in which its working agrees with, or differs from, those of the polytechnicums, e.g., of Zurich and Aachen.

Detection of Fluorine in Bones Recent and Fossil.
—Ad. Carnot.—In recent bones calcium fluoride is present in small proportions; 0.35 in a human thigh-bone, 0.45 in the thigh-bone of an ox, 0.63 in the thigh-bone of a sea-cow, and 0.20 in the tusk of an elephant. In fossil bones the proportion of fluorides is much larger. Thus the bones of a sea-cow from the deposits of Charlestown contained 6.21 calcium fluoride, the tusks of *Elephas Meridionalis* from the Pliocene of Saint-Prest 4.22, and the tusks of the mastodon of Simorre contain 5.30 per cent of calcium fluoride. The author is of opinion that this excess is due either to infiltrations containing traces of alkaline fluorides or to a slow transference of calcium fluoride derived from adjacent minerals.—*Comptes Rendus*, cxiv., No. 21.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 19th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Arthur Edward Barrows, Bloomfield Iron Works, Tipton, Staffs.; Horatio Ballantyne, 269, Renfrew Street, Glasgow; Thomas Cockerill, 105, Derby Street, Bolton; John Evans, Treas. R.S., Nash Mills, Hemel Hempstead; John Gibson, Ph.D., 15, Hartington Gardens, Edinburgh; Henry Ramsden Redman, 10, the Gardens, East Dulwich, S.E.

The President announced that the Council at their meeting that afternoon had adopted the following resolution expressive of the loss the Society and chemists generally had suffered by the death, on May 5, of Professor von Hofmann. The resolution would be communicated to the family of the deceased and to the German Chemical Society:—

The President and Council of the Chemical Society, at their first meeting since the death of their illustrious colleague Augustus William von Hofmann, desire to record their sense of his eminence and of the great scientific work he achieved both in England and in Germany.

Invited to London in 1845 to organise and superintend the Royal College of Chemistry, he spent nearly twenty years in this country, and during that time made many brilliant discoveries, and trained a body of investigators who have followed his example in extending the bounds of the science and in applying chemical principles to the industrial arts.

"Many of the Fellows of the Chemical Society were introduced by him to the science, and look back with gratitude to his inspiring teaching.

"Hofmann's influence on science in this country still remains, though the country of his birth has, since 1865, received the immediate benefit of his personal labours as an investigator, teacher, and organiser.

"The President and Council of the Chemical Society of London desire to express to their colleagues of the German Chemical Society their profound sorrow at the death of the great chemist so closely connected with both, and their sympathy with the sister Society in the loss of its distinguished President."

Of the following papers those marked * were read:—

* 16. "The Magnetic Rotation of Compounds supposed to contain Acetyl or of Ketonic Origin." By W. H. PERKIN, Ph.D., F.R.S.

The author, after referring to the diverse views which are held as to the constitution of ethylic acetoacetate, draws attention to Bruhl's determination of the refractive powers of this substance, which favours a ketonic constitution, and to its magnetic rotation, which was determined several years ago by himself, and which also supports this view; a list is then given of seven acetyl compounds of which he has ascertained the magnetic rotations, all giving numbers pointing to a ketonic constitution. But as such compounds behave sometimes as ketonic and sometimes as hydroxy-derivatives, it was thought desirable to examine a larger number of compounds supposed to contain acetyl or of ketonic origin under different circumstances; the following were selected:—Pyruvic acid; levulinic acid, fused and in solution; ethylic acetonediacarboxylate; ethylic acetoacetate; acetylacetone; methylacetylacetone; ethylic β -amidocrotonate. The last-mentioned four were examined at widely different temperatures.

The rotation of the first five compounds gave numbers corresponding to a ketonic constitution, though those obtained with ethylic acetonediacarboxylate were rather

high, and it is therefore proposed to re-examine this substance at higher temperatures.

The rotation of acetylacetone was found to be very high, showing it to be an unsaturated or hydroxy-compound, whilst the value obtained for methylacetylacetone stands between the hydroxy- and ketonic rotations. At temperatures approaching that of boiling water, it was found, however, that these compounds give much lower rotations than when cold: in the case of the former, the values fall between the hydroxy- and the ketonic rotations, and in the case of the latter, they nearly correspond to the ketonic rotation, showing apparently that they change into the more stable or ketonic form when heated. The refractive and dispersive powers of the same compounds, determined at different temperatures, confirmed the magnetic rotations.

The magnetic rotatory power of ethylic β -amidocrotonate was found to be remarkably high, as was its refractive and dispersive power, showing it to be an unsaturated compound; the author proposes to continue the examination of substances of this class.

DISCUSSION.

Dr. COLLIE remarked that he had long held the view that ethylic β -amidocrotonate was an imido-derivative, the correctness of which appeared to be demonstrated by Dr. Perkin's measurements.

Dr. PERKIN, in answer to Dr. Morley, said that he had not yet ascertained whether acetone was abnormally affected by heating.

*17. "The Origin of Colour. II. The Constitution of Coloured Nitro-compounds." By HENRY E. ARMSTRONG.

In a communication to the Society in March, 1888 (*Proceedings*, 1888, 27), in which the relation between colour and constitution was discussed, it was maintained that in the case of azo-dyes, the rosanilines, methylene-blue, &c., colour was conditioned by a quinonoid structure. Although the general correctness of this view has never yet been acknowledged, a study of the literature relating to coloured compounds which has appeared in the interval clearly shows that it is more and more recommending itself; it should also be mentioned that Nietzki, in the introduction to his *Organische Farbstoffe* (Berlin, 1889), makes reference to the quinonoid character of a number of dye-stuffs, although he does not seek to apply such a view of their structure at all generally. The subject has continually occupied my attention since I first brought it before the Society, and I think it is justifiable that I should now state the opinion at which I have arrived; viz., that in the case of coloured compounds which have been fairly well studied, it is so generally true that a quinonoid formula is applicable, that the reconsideration of the formula of any coloured substance is warrantable if it do not come within the rule. The term "quinonoid" must, however, be understood to include compounds of the type of benzyl; and it is to be noted that in the case of closed chain compounds, it appears to be essential that at least one of the quinonoid carbon atoms be associated with a dyad radicle, and that the ring itself be unsaturated; the presence of two ortho- or para-carbonyl groups in a saturated ring apparently does not condition colour.

Nitro-compounds have from an early period attracted my attention, as they do not come within the suggested "colour rule." It is well known, however, that nitro-compounds are not all coloured, many which are commonly described as yellow being obtained white when prepared from pure materials, and precaution is taken to remove the phenolic compounds which are so frequently formed even from hydrocarbons during nitration; from this it follows that the nitro-group does not *per se* condition colour. A comparison of ortho- with paranitrophenol affords striking confirmation of the correctness of this conclusion: the former alone is coloured, being intensely yellow, very volatile, and insoluble in water; whereas paranitrophenol does not volatilise with steam,

and is fairly soluble in water. To what is the difference ascribable? It can scarcely be otherwise than to a difference in structure beyond that involved in a mere difference in the relative positions of the radicles. Dr. Kipping and I, in the course of an investigation of coloured nitro-compounds in which we are engaged, have had occasion to compare the methoxynitrobenzenes prepared from ortho- and para-nitrophenol, and we find not only that they are *both* colourless, but that they agree as closely in their general properties as do most isomeric compounds containing the same radicles; it is particularly noteworthy that they are about equally volatile with steam. The non-correspondence of the two nitrophenols is rendered far more striking by the correspondence of the compounds prepared from them by methylation, and the conclusion is strengthened thereby that they are not mere position isomerides: it therefore appears justifiable to represent orthonitrophenol by a quinonoid formula, which may readily be done by transferring the hydroxylic hydrogen to the NO_2 group, thus transforming it into a dyad group, NO_2H , a change which admittedly attends the formation of so-called nitrosophenol (quinonehydroxime) (*cf.* Nietski, *op. cit.*, p. 9). On this hypothesis, the name *quinoneorthonitroxime* may be suggested for "orthonitrophenol."

Paranitrophenol, although itself colourless, yields coloured metallic derivatives, in the formation of which a change of structure must be involved, according to the view here advocated.

As only para- and ortho-compounds can have quinonoid formulæ, it would follow that metanitro-derivatives must be colourless; but actually metanitriline has an intense yellow colour. There are but two ways out of this difficulty: to assume that metanitriline either is not (as ordinarily obtained) a uniform substance, or that its structure is not really that of an amidonitrobenzene. There is, however, no obvious other mode of representing it; and although Dr. Kipping and I have spent much time in trying to deprive it of its colour, we have been unsuccessful; we have found, however, that it yields a practically colourless benzoate, a result which we regard as strong presumptive proof in favour of the view that metanitriline is not what it is supposed to be, and we therefore propose to submit it and similar compounds to exhaustive study.

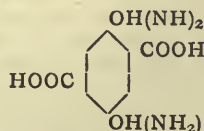
If it be granted that in the case of ortho- and paranitrophenol there may be a transference of hydrogen or metal to the NO_2 group, leading to the formation of nitroximes, it is conceivable that a similar change may take place in other cases; for example, in the case of the primary nitroparaffins, the properties of which are in many respects compatible with the view that they are nitroximes. Moreover, the explanation would gain support which is afforded of the "acid" properties manifested by a compound such as benzyl cyanide, by regarding it as, at least potentially, an imide $\text{C}_6\text{H}_5\text{CH}_2\text{C:NH}$.

A consistent explanation of the formation of metallic derivatives could be given, and it would be unnecessary to assume that "hydrocarbon" hydrogen other than acetylenic is displaceable by metal, if the view here suggested were accepted.

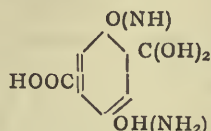
*18. "The Origin of Colour. III. Colour as an Evidence of Isodynamic Change: the Existence of Isodynamic Acids." By HENRY E. ARMSTRONG.

The application of the colour-rule dwelt on in the foregoing note must lead not only to the modification of many of the formulæ attributed to coloured substances, but also to the recognition of equivalent or *isodynamic* forms (*cf.* Morley and Muir's "Watts' Dictionary of Chemistry," iii., Art. "Isomerism") of a variety of compounds, as I have already partially indicated. Thus it appears to me to be impossible any longer to regard the coloured substances known as paradihydroxyterephthalic acid, dihydroxyppromellithic acid and the corresponding "diamido-" acids (*cf.* Nef, *Annalen*, cxxxvii., 38) as con-

stituted in the manner suggested by these names, and there is no difficulty in representing them as quinonoid compounds, thereby accounting for their being coloured, thus:—



Dihydroxy-
Diamido- } terephthalic acid.



Isodynamic form of
Dihydroxy-
Diamido- } terephthalic acid.

In principle this idea is not novel (*cf.* Hantzsch and Herrmann, *Ber.*, 1887, 2800; indeed, it has already been rejected (Baeyer, *Annalen*, cxxlv., 189; Nef, *ibid.*, cclviii., 261), but on grounds which I regard as altogether insufficient, holding, as I do, the opinion that the character of such substances is scarcely to be determined by purely chemical methods, owing to the readiness with which a change in type sets in. This is well illustrated in the case of the ethylic salts of "diamido-" terephthalic and pyromellithic acids, which are both red-coloured substances, but yield colourless salts with acids, the addition of HCl being sufficient, it would seem, to suppress the chromophoric group $C(NH_2) \cdot C(OH)(OEt)$, which becomes $C(NH_2 \cdot HCl) \cdot COOEt$, so that in presence of acids such substances would tend to behave as amido-compounds.

If it be surmised on the evidence afforded by colour that acids exist which are not true carboxylic, but *carbhydrilic*, acids, there is no reason to deny the possible existence of such acids among colourless compounds, and it is conceivable that some of the reputed geometrically isomeric acids are of this character; von Baeyer's two hexahydroterephthalic acids perhaps afford an example of such isomerism. At present, however, we have no means of differentiating such acids from carboxylic acids.

There are a number of cases in which a suggestive explanation of peculiarities may be given with the aid of the hypothesis advocated in these notes. Thus, although orthonitromethoxybenzene is colourless when solid, the fused substance is yellow; if not due to the presence of impurity, or to slight decomposition, the appearance of colour in such a case may be conditioned by the occurrence of isodynamic change on heating. Then it is conceivable that the slight intensity in the colour exhibited by some substances may be due to the fact that the coloured and colourless isodynamic forms are both present, the coloured form in but small amount. On this view, it would be possible to understand the marked difference in intensity of colour sometimes apparent between derivatives of a coloured substance. Thus, in the case of the substituted nitrophenols, the silver derivative has frequently a much deeper colour than the potassium derivative; and the metallic derivatives of iododiorthonitrophenol are crimson, while those of the corresponding chloro-compound are bright-red; it may be that one metal more than another, and one halogen more than another, favours the occurrence of the isodynamic change on which the colour is dependent.

DISCUSSION.

Dr. ARMSTRONG, in reply to a remark by Professor Ramsay, said that although it was true that all substances exhibited absorptive power in some region of the spectrum, it was a remarkable fact that compounds which are coloured in the conventional sense clearly differ in constitution from colourless compounds, and it therefore appeared justifiable to discuss the origin of visible colour apart from the general question of absorption. It was very noteworthy that saturated compounds had but slight absorptive power even for invisible rays, and there appeared to be a connexion between the power of exercising selective absorption and what has been termed

residual affinity: so much was this the case, that it appeared probable to him that ultimately colour would be traced to that peculiar condition represented conventionally by a double bond, the atoms being regarded as altogether subordinate.

(To be continued.)

NOTICES OF BOOKS.

Mineralogy. By F. H. HATCH, Ph.D., F.G.S. (of the Geological Survey of England and Wales). London: Whittaker and Co., and G. Bell and Sons, 1892. (Small 8vo., pp. 124).

In his preface the author notices the undeniable fact that mineralogy is now no longer in Britain at least a favourite pursuit. This present neglect is, he thinks, in part due to the predominant interest taken in biology. We are not sure that he is correct in his judgment. It seems to us that the declining popularity of mineralogy may be traced further back than the Darwinian avatar. In any case the science seems to find more cultivators in America and in France than in England.

Dr. Hatch has certainly done justice to his subject, and it is perhaps not too much to hope that his treatise may contribute to effect a revival of the study of mineralogy among us. The work is divided into two parts, the first treating of form, chemical composition, specific gravity, hardness, cleavage, fracture, and the optical phenomena of minerals: not, however, including double refraction and polarisation.

The second part is taken up with the classification and description of minerals. He seems to prefer a classification of minerals into rock-formers, ores, salts, and useful minerals other than ores, and lastly precious stones. Thus his arrangement is neither chemical nor crystallographic, but we might perhaps say utilitarian, which may possibly suit the tastes of the age. Among the useful minerals overlooked are bauxite, cryolite, and chrome iron. Some of the localities given would be improved by revision. Thus, as a locality for graphite, we find no mention of Ceylon. No locality is given for asbestos, which is merely tabulated among the hornblendes.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 21, May 23, 1892.

Combustion- and Formation-Heats of Alcohol, and of the Formic and Acetic Acids.—MM. Berthelot and Maignon.—This paper does not admit of useful abstraction.

Certain Facts concerning the Chemical History of Nickel.—P. Schutzenberger.—According to the most recent researches, the atomic weight of nickel seems definitely fixed at 58.6. An occlusion of oxygen is observed in a constant manner with nickel oxide calcined at white redness and finely pulverised. The greenish-yellow oxide, moderately calcined, does not present it, no more than does cobalt oxide strongly calcined. Reduced nickel obtained from the strongly calcined oxide, instead of becoming agglomerated under the influence of heat into a single mass of a metallic lustre, remains in the state of a dull, dark grey powder.

Soft Tempered Sulphur in the State of Vapour.—Jules Gal.—Sulphur, strongly heated, absorbs a certain quantity of heat, and passes into the insoluble state. A

similar absorption of heat, and a similar transformation, ought to ensue if the sulphur is evaporated, so that soft sulphur is obtained on receiving the vapours of sulphur on the surface of a cold liquid. The experiment succeeds equally well if we use as a tempering bath water, nitric acid, more or less dilute, hydrochloric acid, or a solution of soda, but it succeeds very badly with ammonia. The soft sulphur thus obtained has a peculiar aspect, in thin plates, and of a light yellow colour very different from the colour of ordinary sulphur. If examined with the microscope it appears formed of rounded grains, transparent, and cemented together in ramified reticulations. It is formed of a mixture of soluble and insoluble sulphur, but the insoluble sulphur extracted from it appears intermediate between those obtained from ordinary soft sulphur and from flowers of sulphur. If it is heated to 100° for one hour, 13·6 per cent remains in the insoluble state as compared with 0·3, the quantity obtained from ordinary soft sulphur, or 23, which is the yield from flowers of sulphur. The proportion of insoluble sulphur contained in soft sulphur, tempered in the state of vapour, varies with circumstances, especially with the temperature of evaporation. Below 200° it is very difficult to give numbers, for the vapour even if conducted by a gaseous current is inconsiderable, and the laminæ are formed very slowly. At higher temperatures the percentage of insoluble sulphur varies from 18 at 215°, to 37 at 320°.

Certain Basic Nitrates.—G. Rousseau and G. Tite. —Many basic salts have been prepared by heating the solutions of the corresponding neutral salts in sealed tubes in presence of an agent capable of saturating the free acid as it is separated, but the precipitates formed are often amorphous. To obtain crystalline deposits it is necessary to use not saline solutions but solid neutral hydrates whenever they are capable of undergoing aqueous fusion. The neutral nitrates examined have all behaved conformably to expectation except silver nitrate, which strongly attacks glass, forming a nitro-silicate. In all the experiments neutral hydroxides containing 6 mols. of water were heated to temperatures from 100° to 350°. Except in case of calcium nitrate where caustic lime was employed, the authors added small fragments of marble along with the solid hydrates. By operating in this manner the authors obtained basic nickel nitrate, $5\text{NiO}, \text{N}_2\text{O}_5, 4\text{H}_2\text{O}$, basic zinc nitrate, $5\text{ZnO}, \text{N}_2\text{O}_5, 6\text{H}_2\text{O}$, basic cadmium nitrate, $5\text{CdO}, 2\text{N}_2\text{O}_5, 8\text{H}_2\text{O}$, and a basic lime salt, $2\text{CaO}, \text{N}_2\text{O}_5, 2\text{H}_2\text{O}$.

Preparation and Properties of Arsenic Cyanide.—E. Guenez. —The author causes cyanogen iodide to react upon free metallic arsenic. The compound obtained, AsCy_3 , is a yellowish powder of a crystalline texture. It is decomposed instantly by water, which resolves it into arsenic and hydrocyanic acid.

Apocinchonine and Diapocinchonine.—E. Jungfleisch and E. Léger. —On heating cinchonine with hydrochloric acid of specific gravity 1·125 from 140° to 150° for 6 to 10 hours, Hesse obtained two bases which he described as apocinchonine and diapocinchonine. The authors find that diapocinchonine is a mixture and not a definite principle. The action of hydrochloric acid upon cinchonine produces the same isomers as that of sulphuric acid.

Monosodic Pyrocatechine.—M. de Forcrand. —A thermo-chemical paper, which does not admit of useful abstraction.

Substitutions Linked to Carbon and to Nitrogen. Application to Explosive Compounds.—C. Matignon. —Not suitable for abstraction.

Bibromomalonic Acid.—G. Massol. —Also a thermo-chemical paper not admitting of useful abstraction.

Detection of Higher Alcohols in Ethylic Alcohol.—C. Bardy. —(See p. 283).

On a Tetramethylmetadiamidobenzidine.—Charles Lauth. —Not adapted for abstraction.

Journal für Praktische Chemie.
 New Series, Vol. xlv., Parts 2 and 3.

Communication from the Chemical Laboratory of the Clark University, Worcester, Mass., U.S.A.—Massuo Skuta. —This memoir on the action of acet-acetic ether upon quinones, and on the synthesis of benzofuran derivatives seems to have already appeared in an English version.

Synthesis of Oxygenous Derivatives of Pyrazol.—L. Lederer. —This paper is chiefly devoted to a comparison of the reactions of antipyrin and isoantipyrin.

Determination of Sulphur in Inorganic Sulphides by Decomposition in a Current of Oxygen at a Red Heat, and Reception of the Products of Oxidation in a Solution of Hydrogen Peroxide. Analysis of Molybdenite, Realgar, and Orpiment.—P. Jannasch and V. Wasowicz. —This memoir will be inserted in full as early as possible.

(1) **Simple Methods for the Quantitative Analysis of Galena. Analysis in the Moist Way by means of Bromine.**—P. Jannasch and K. Aschoff.

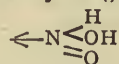
(2) **Analysis of Galena in the Moist Way by Precipitating the Lead with Hydrogen Peroxide in an Ammoniacal Solution.**—P. Jannasch and Th. Bickes.

(3) **Analysis of Galena in the Dry Way by Ignition in a Current of Air Saturated with Bromine.**—P. Jannasch and Th. Bickes. —These three methods will be given in full.

Communications from the Laboratory of Prof. Flawitsky, at Kasan.—These communications comprise a paper by F. Flawitsky on the "Dextrorotatory Terpene from the Needles of the Siberian Cedar" (*Pinus cembra*), and a memoir by B. Kuriloff on the "Terpenes from the Resin of *Pinus Abies*."

Introduction to an Accurate and Convenient Method of Determining Vapour Densities, even at Greatly Reduced Pressures.—C. Schall. —This memoir requires the three accompanying diagrams.

The First Stages of Reduction of the Nitro-group.—C. Willgerodt. —Substances of the first stage of reduction of the nitro-compounds are either dihydronitro-compounds distinguished by the group—



and the two nitroso-substances derived from them, in which the group $\text{N}=\text{O}$ is directly attached to the carbon, or products of condensation formed by the reduction of two nitro-mols. The compounds of the second stage of reduction may be simple or condensed. The author's relations with the German Chemical Society seem to be in an unpleasant state of tension.

Certain Salts of Hypophosphoric Acid.—C. Rammeisberg. —(This paper, though communicated by the author, has already appeared in the *Transactions of the Royal Prussian Academy of Sciences*). We have here an account of lithium hypophosphite, normal and acid, of thallium hypophosphite, normal and acid, and of the barium, magnesium, glucinum, silver, and lead salts.

Revue Universelle des Mines et de la Metallurgie.
 Series 3, Vol. xvii., No. 3.

This issue does not contain any chemical matter.

Series 3, Vol. xviii., No. 1.

The Borax of California.—From the CHEM. NEWS.

The Spontaneous Combustion of Coal.—From the *Proceedings of the British Association* at the Cardiff Meeting, 1891.

MISCELLANEOUS.

HIGH COURT OF JUSTICE.

TUESDAY, MAY 31, 1892.

QUEEN'S BENCH DIVISION.

Before the LORD CHIEF JUSTICE.

JOHNSTONE v. TILDEN AND OTHERS.

Mr. Jelf, Q.C., Mr. Pocock, and Dr. B. O'Connor (instructed by Mr. J. P. Godfrey) appeared for the Plaintiff. *The Solicitor-General* (Sir Edward Clarke, Q.C.) and *Mr. Boydell Houghton* (instructed by Messrs. Markby, Stewart, and Co.), appeared for the Defendants.

(Transcript from Shorthand Writer's Notes).

The SOLICITOR-GENERAL—Will your Lordship forgive my interposing for the moment during the hearing of another case to relieve your Lordship's list of a case which we shall not have to trouble the jury with? It is the case of *Johnstone v. Tilden* and others, and my learned friend Mr. Jelf, who appears for the plaintiff, wishes to say a few words.

The LORD CHIEF JUSTICE—Certainly.

Mr. JELF—If your Lordship thinks that I am not unduly interfering with the case that is now on, to suit the Solicitor-General and my convenience, I should like to mention this case now. I appear for the plaintiff, Dr. Johnstone, with my learned friends Mr. Pocock and Dr. O'Connor. It is an action brought by the Doctor against the Institute of Chemistry of Great Britain and Ireland, represented here by my learned friend the Solicitor-General. The action was brought to prevent the Institute from persevering in excluding him from being a Member and Fellow of the Institute upon a certain charge of unprofessional conduct which had been made against him. My Lord, I have very carefully considered the facts, and the evidence on which this case was sought to be based, and although my client was very desirous of clearing his character as much as he possibly could, I pointed out to him that their Charter gave the Institute very large powers, so long as they were acting in good faith and in accordance with their rules, in deciding rightly or wrongly on the matters brought before them. My client has, I hope wisely, placed himself in my hands in the matter, and in accordance with what has passed between the Solicitor-General and myself, we have agreed, with your Lordship's permission, to deal with the case by making a short statement on each side. On the part of the plaintiff, I desire to withdraw unreservedly any suggestion that these gentlemen have been acting otherwise than in good faith and in accordance with the rules of the Institute. On the other hand, I am glad to say that the Solicitor-General sees his way to saying this on behalf of the gentlemen whom he represents: "That their action was founded entirely on their view of the professional conduct of the plaintiff on a single occasion, and involved no imputation upon his character or professional capacity." Two views might possibly be taken of the question that was at issue; but looking to the circumstances of the case, and, it seems to me, the very handsome way I have been met by the Solicitor-General, with the consent of his clients, I think it would be extremely unwise for my client to fight for more than he has received. Under these circumstances, we have agreed, with your Lordship's consent, to withdraw the record, and meanwhile the Plaintiff undertakes to give up any title he might have had to be a Fellow or Member of the Institute, and to hand over what perhaps I cannot say that my client is entitled to keep, but no doubt he will do what is right,—he will not persist in representing himself as a member of the Institute, and he will hand over his documents.

The SOLICITOR-GENERAL—I am much obliged to your Lordship for allowing me to interpose. Representing the

authorities of the Institute of Chemistry, my only desire is to make it perfectly clear, and it is their only wish to make it clear, that they acted throughout deliberately and in the exercise of the deliberate judgment vested in them, and according to the Rules of the Institute to which the Plaintiff himself belonged. The words my learned friend has read are words that I agree to; I agree that there might be some controversy and difference of opinion as to the action of the Plaintiff himself, which was brought under the notice of the defendants, but it was carefully considered by them; they took the course they were bound to take in the interests of their profession, and I am glad to have the opportunity of saying not only that they have acted regularly in the manner, but they are anxious their action should not be taken to carry with it an imputation which it really ought not properly to bear. It was a question of professional conduct in a single instance and their action upon it, and that action they were obliged to notify. In this case, my Lord, we have agreed to the record being withdrawn with your Lordship's permission.

Mr. JELF—And no costs.

The LORD CHIEF JUSTICE—I can only give effect to the desire of the parties and the record may be withdrawn.

NOTES AND QUERIES.

* * * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"The Chemist."—Mr. J. Cathbert Welch will find full bibliographical details of "The Chemist" published in the *CHEMICAL NEWS*, vol. li., p. 304 (June 26, 1885). He will also find the dates of every volume of the same journal on p. 662 of my "Catalogue of Scientific and Technical Periodicals," published in the "Miscellaneous Collections of the Smithsonian Institution," (No. 514), Washington, 1885.—H. CARRINGTON BOLTON.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Chemical Industry, 8. "Oil-Gas," by Prof. V. B. Lewes. "The Soluble Bituminous Constituents of certain Japanese Coals," by Watson Smith.

TUESDAY, 14th.—Royal Medical and Chirurgical, 8.30.

WEDNESDAY, 15th.—Meteorological, 7.

Microscopical, 8.

THURSDAY, 16th.—Royal, 4.30.

Chemical, 8. Ballot for the Election of Fellows. "Contributions to an International System of Nomenclature—The Nomenclature of Cycloids," by Dr. H. E. Armstrong. "The Production of Pyridine Derivatives from the Lactone of Triacetic Acid," by Dr. N. Collie.

FRIDAY, 17th.—Quekett Club, 8.

THE CHEMICAL NEWS

AND

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THE CHEMICAL NEWS.

VOL. LXV., No. 1699.

THE QUALITATIVE DETECTION OF NICKEL AND COBALT.

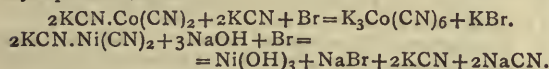
By FRED. J. HAMBLY,

Assistant Lecturer and Senior Demonstrator in Chemistry,
University College, Dundee.

THE qualitative detection of nickel in presence of cobalt is often a difficulty with the beginner in the study of analysis. When the conditions are correctly understood, Liebig's cyanide separation,—the essential details of which were fully worked out by Gauhe (*Zeit. für Anal. Chem.*, 1866, p. 75) in 1866,—is, in the writer's experience, the simplest and most rapidly executed. Although clearly stated by Fresenius in his "*Quantitative Analysis*,"* so far as I am aware, there is not one of all the multitude of text-books on qualitative analysis in our language which recommend this method that does not introduce some unnecessary condition into the procedure, and in most cases the student's difficulties arise not from his own incapacity, but from the faulty description given by his text-book.

Although the subject is not original, it may therefore be useful to call attention to the simplest and most satisfactory method of working. Gauhe showed conclusively that the conversion of potassium cobaltous cyanide into the cobaltcyanide by boiling with hydrocyanic acid (at best a dangerous experiment), is always incomplete; but that by means of a suitable oxidising agent, in alkaline solution the cobalt may be directly converted into the soluble cobaltcyanide, the nickel being simultaneously precipitated as hydrated nickelic oxide. The method of detecting nickel in presence of cobalt is then as follows. Separate the mixed sulphides from the ammonium sulphide precipitate by means of cold dilute hydrochloric acid, and test a small portion in a borax bead. The presence or absence of anything more than a trace of cobalt is directly indicated by the colouration produced. Dissolve the sulphides in hot hydrochloric acid with the aid of potassium chlorate, boil off the excess of chlorine, and remove the excess of acid either by neutralisation or evaporation to dryness. To the neutral solution add an excess of freshly prepared solution of potassium cyanide in cold water, beyond what is necessary to re-dissolve the precipitated cyanides. Boiling is unnecessary. Make the solution decidedly alkaline with sodium hydrate, add about twice the volume of bromine water, heat gently, allow to stand a few minutes, and filter off the precipitated nickelic oxide. The nickel may be confirmed by the borax bead reaction after washing the precipitate.

The action of the oxidising agent can be represented by equations, thus—



There is no liberation of hydrocyanic acid at any stage of the process, so the operations may be safely conducted in the open laboratory. Commercial cobalt salts almost invariably give a precipitate of nickelic oxide. The cyanide method has the advantage over the precipitation of the cobalt as potassium cobaltinitrite, in that the separation is most frequently carried out with the object of detecting nickel, which metal is immediately separated as a precipitate readily available for examination.

If the analysis is to include a search for traces of

cobalt, the alkaline filtrate from the nickel precipitate is, in the draught cupboard, acidified with excess of sulphuric acid, and evaporated until the excess of acid is nearly expelled. The residue is taken up with water, made alkaline with ammonia, the cobalt, if present, precipitated by ammonium sulphide, and confirmed by the borax bead. Or, a portion of the neutral solution, containing the nickel, may be treated with acetic acid and potassium nitrite, and the traces of cobalt directly precipitated by allowing to stand for a few hours.

A NEW GASEOUS INCANDESCENT LAMP.

By H. N. WARREN, Research Analyst.

THE incandescent property of platinum in most of its allotropic modifications has been noted from an early period, but as regards brilliancy is far inferior to such substances as, for instance, magnesia, lime, asbestos, and lastly zirconia.

To thus obtain a suitable thread material in order to present a substance to work a film from, probably no substance is better suited than asbestos itself, both on account of its indestructibility and also as regards its compactness and inferior conductivity of heat; but, on the other hand,



asbestos possesses none of the properties of platinum with respect to incandescence. True platinised asbestos prepared by immersing asbestos fibre in solution of platinum chloride has been, and still is, frequently employed to promote catalysis or surface action, but in comparing its value as a lighting agent it scores very low. In this case the decomposition of the platinum salt employed destroys by rendering rotten the fabric of the asbestos, and to overcome this difficulty the author has contrived and succeeded in combining a special combination of platinum not hitherto noted in conjunction with zirconia. The film thus employed is mounted inside the small globe, as shown by the accompanying diagram, which represents two lamps, namely, A and B, which are readily connected to each other by the short tube, C, the bottom lamp, B, being connected at D with a gas supply arranged to admit of a supply of air and gas as through an ordinary Bunsen burner, the uppermost pipe, E, intended to convey

* Seventh English Edition, vol. i., p. 444. In his "*Qualitative Analysis*" Fresenius adopts the more tedious nitrite separation.

the waste gases through a suitable aperture into the open. The ignition of the film is readily brought about by applying a heated wire during the passage of the gas, and provided the gas and air supply are kept constant, several such lamps may be fed from the one gas supply.

For advertising purposes an ingenious modification of this in the form of large letters has been constructed, in which words may be maintained at a white heat, and observable at great distances. With this second invention there are still some difficulties to overcome, but by its aid the writer hopes before long to bring to the front one of the latest advertising freaks.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

REMARKS ON THE MANUFACTURE OF CRUCIBLE STEEL IN RUSSIA.

By SERGIUS KERN, M.E., St. Petersburg

(Continued rom p. 170).

IV.—On the Uses of Steel.

BESIDES making tool steel and casting chrome steel projectiles by the process worked out by the French workers, J. Holtzer, Unieux, Loire, we made steel for car and engine tyres for some Government special trains. We used a mixture of Beloretz puddled steel, cast-iron, and turnings resulting from the treatment of the projectiles in the mechanical shop.

Owing to this fact a certain quantity of chromium was always present in the steel for tyres. Ordinarily we had about 0.30 per cent of chromium in the metal. This quantity, however small, has a marked good influence on the metal, raising its tenacity. The test pieces taken out of the tyres gave on the average an elongation of 22–25 per cent in a length of eight inches.

The quantity of different elements in the tyre steel was as follows:—

Carbon (total)	0.45 per cent.
Manganese	0.18 "
Silicon	0.20 "
Sulphur	0.02 "
Phosphorus	0.03 "
Chromium	0.26 "

It is striking that such small quantities of chromium, as already observed by many engineers, produce such a good effect on steel, making the metal highly tenacious. A specimen tyre stood without cracking forty drops of a 15-pood monkey, being bent at last to the form of cipher 8.

The tool steel of the Poutiloff Iron and Steel Works is readily ordered by many railways and railway works. At the Works all the turning of hardened rolls, for their rail, beam, and plate trains is done by their own steel. The steel is made from a mixture of Beloretz puddled steel and cast iron, and contains about 1.25 per cent of carbon and 0.12 per cent of manganese.

Certain engineers advocate the use of large ingots for the manufacture of tool steel. They are hammered and rolled, and the resulting bars after inspection (flaws and cracks are chiselled out), are finished under quick working hammers down to the size demanded.

We used small ingots as mentioned in our previous paper; the same is done in most works abroad. It is easier to inspect a small ingot before sending it to the hammer, and next the evil of internal strains, which are constantly present in big ingots, is nearly avoided by the use of ingots of small dimensions.

In a further paper I propose to deal with the manufacture of projectiles in Russia. Several works here make capital artillery pieces, which were formerly obtained abroad.

METHODS OF ANALYSIS OF DAIRY PRODUCTS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Continued from p. 281).

ALTERNATE METHOD OF DETERMINING VOLATILE ACIDS.

Saponification without the Use of Alcohol.

To avoid the danger of loss from the formation of ethers and the trouble of removing the alcohol after saponification, the fat may be saponified with a solution of caustic potash in a closed flask without alcohol. The operation is carried on exactly as indicated above for saponification in a closed flask, using caustic potash solution instead of soda, and omitting the operation for volatilising the alcohol. The caustic potash is prepared as follows:—Dissolve 100 grms. of the purest potassium hydrate in 58 grms. of hot distilled water. Allow to cool in a stoppered vessel, decant the clear caustic solution, and preserve in a vessel out of contact with the air. For the saponification use 2 c.c. of the caustic potash solution, which is poured on the fat after it has solidified in the flask. Great care must be taken that none of the fat is allowed to rise on the sides of the saponifying flask to a point where it can not be reached by the alkali. During the process of saponification the flask can only be very gently rotated in order to avoid the difficulty mentioned above. This process is not recommended in any except a closed flask with round bottom. In the subsequent solution of the soap, use only 80 c.c. of distilled water, and in setting free the fatty acids use 60 c.c. of the dilute sulphuric acid. In other respects the distillation is conducted as described. Potash is used instead of soda, so as to form a softer soap, and thus allow a more perfect saponification.

The saponification may also be conducted as follows:—The alkali and fat in the melted state are shaken vigorously in the saponification flask until a complete emulsion is secured. The rest of the operation is then conducted as above.

Iodine Equivalent.

Reagents.

1. Dissolve 25 grms. of pure iodine in 500 c.c. of 95 per cent alcohol. Dissolve 30 grms. of mercuric chloride in 500 c.c. of 95 per cent alcohol. The last solution, if necessary, is filtered, and then the two solutions mixed. The mixed solution should be allowed to stand twelve hours before using.

2. *Decinormal Hyposulphite of Sodium Solution.*—Take 24.6 grms. of chemically pure hyposulphite of soda freshly pulverised as finely as possible and dried between filter or blotting paper. Make this up to 1000 c.c. at the temperature at which the titrations are to be made.

3. *Starch Paste.*—One gm. of starch boiled in 200 c.c. of distilled water for ten minutes, and cooled to room temperature.

4. *Solution of Iodide of Potassium.*—150 grms. of iodide of potassium dissolved in water and made up to 1 litre.

5. *Solution of Bichromate of Potassium.*—Dissolve 3.874 grms. chemically pure bichromate of potassium in distilled water, and make the volume up to 1 litre at the temperature at which the titrations are to be made.

Manipulation.

Standardising the Hyposulphite of Sodium Solution.—Run 20 c.c. of the bichromate of potassium solution into a glass stoppered flask to which has been added 10 c.c. of the solution of iodide of potassium. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of hyposulphite of sodium to flow slowly into the flask until the yellow colour of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the hyposulphite of sodium solution until

the blue colour just disappears. The number of c.c. of hyposulphite solution used multiplied by 5 is equivalent to 1 grm. of iodine.

Example.—20 c.c. $K_2Cr_2O_7$ solution required 16.2 c.c. hyposulphite of soda; then $16.2 \times 5 = 81 =$ number c.c. of hyposulphite solution equivalent to 1 grm. of iodine. Then 1 c.c. of hyposulphite solution = 0.0124 grm. of iodine. Theory for decinormal solution of hyposulphite of sodium, 1 c.c. = 0.0127 grm. of iodine.

Weighing the Sample.—About 1 grm. of butter fat is to be weighed in a glass stoppered flask holding about 300 c.c., with the precautions mentioned for weighing the fat for determining volatile acids.

Absorption of Iodine.—The fat in the flask is dissolved in 10 c.c. of chloroform. After complete solution has taken place, 30 c.c. of the iodine mercuric chloride solution are added. The flask is now placed in a dark place, and allowed to stand with occasional shaking for three hours.

Titration of the Unabsorbed Iodine.—100 c.c. of distilled water are added to the contents of the flask, together with 20 c.c. of the iodide of potassium solution. Any iodine which may be noticed upon the stopper of the flask should be washed back into the flask with the iodide of potassium solution. The excess of iodine is now oxidised with the hyposulphite of sodium solution, which is run in gradually with constant shaking until the yellow colour of the solution has almost disappeared. A few drops of starch paste are then added, and the titration continued until the blue colour has entirely disappeared. Toward the end of the reaction the flask should be stoppered and violently shaken, so that any iodine remaining in solution in the chloroform may be taken up by the iodide of potassium solution in the water. A sufficient quantity of hyposulphite of sodium solution should be added to prevent a re-appearance of any blue colour in the flask for five minutes.

Setting the Value of the Iodine Solution by the Hyposulphite Solution.—At the time of adding the iodine solution to the fats, two blank flasks of the same size and nature as those used for the determination should be employed for conducting the operation described above without the presence of any fat. In every other respect the conduct of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used.

EXAMPLE.

Blank Determinations.

1. 30 c.c. iodine solution requires 46.4 c.c. hyposulphite of sodium solution.
 2. 30 c.c. iodine solution requires 46.8 c.c. of hyposulphite of sodium solution.
- Mean 46.6.

Percentage of Iodine Absorbed.

Weight of fat taken	1.0479 grms.
Quantity of iodine solution used	30 c.c.
Hyposulphite equivalent of iodine used	46.6 "
Hyposulphite to oxidise remaining iodine	14.7 "
Hyposulphite equivalent to iodine absorbed	31.9 "

Percentage of iodine absorbed, $31.9 \times 0.0124 \times 100 \div 1.0479 = 37.75$ per cent.

Elective Determinations.

For the further study of the properties of butter, the following recommendations are made, to be followed by the analyst or not as he may elect:—

Reduction of Silver.—To determine whether or not the butter has been derived from a cow fed on cotton-seed meal, it will usually be sufficient to test the sample by Bechi's reagent.

The solutions used are as follows:—5 grms. of silver nitrate dissolved in 100 c.c., 95 per cent alcohol, and 1 c.c. of strong nitric acid added. The manipulation is conducted as follows:—Measure out 5 c.c. of the fat into

a small porcelain dish, and add 5 c.c. of the above reagent. Stir together thoroughly with a stirring rod, and place upon the steam-bath for ten minutes. Notice the changes of colour which take place, the intensity of the colour produced, and the amount of silver deposited as a mirror on the sides of the dish.

Reduction Test Applied to the Fatty Acids.—Instead of testing the original glycerides as above, the test may be applied to the fatty acids in accordance with the following directions:—

Reagent.—Dissolve 30 grms. of nitrate of silver in 100 c.c. of water.

Manipulation.—Place 5 c.c. of the fatty acid in the porcelain dish which is used above, and dissolve in 20 c.c. of 95 per cent alcohol. Add 2 c.c. of the reagent, stir thoroughly together, and heat on the water-bath as in the first instance.

Melting-point of the Fatty Acids.—The melting-point of the fatty acids may be determined as described in *Bulletin*, No. 13, Part 4, p. 448.

The melting-point of the fatty acids cannot be determined in the same apparatus and by the same methods as those described for the fats themselves, because the acids are soluble in alcohol. It should be remembered that the melting-point of the fatty acids is slightly above that of the glycerides, and the first determination in every case should be solely for the purpose of determining approximately the temperature at which the fat melts.

The bulb of a delicate thermometer is coated with the fatty acid, and the thermometer by means of a cork is fastened in a round flask of 250 c.c. capacity. The bulb of the instrument should occupy as nearly as possible the centre of the flask. The cork should have an air passage for the equalisation of the pressure. The flask is slowly heated in a current of warm air or otherwise, and as the melting-point is approached a rotary motion is given to it. When the fat melts it is seen to collect in a small drop on the lowest part of the bulb, remaining stationary while the flask is turned. The thermometer is best held horizontally.

Crystallising-point of the Fatty Acids.—The crystallising-point of the fatty acid is determined by means of the method described in *Bulletin*, No. 13, Part 4, p. 447.

A very delicate thermometer with a long bulb is used, the thermometer being graduated to tenths of a degree; the readings of the mercury are made with a small eyeglass. A test-tube about 15 c.m. in length and 2.5 to 3 c.m. in diameter is filled with the melted fatty acids. The temperature at which the acid is melted should be sufficiently high to secure a complete liquefaction. The tube containing the fat is placed in a stopper carried in a bottle so that the whole of the fatty acid may be contained in that part of the tube protected from external currents of air by the bottle. The bottom of this protected bottle should be warm, so that its temperature may be several degrees higher than the crystallising-point of the fatty acid. This precaution is necessary to avoid a too rapid crystallisation of the fatty acid in the bottom of the test-tube, and to secure as nearly as possible a uniform crystallisation throughout the whole mass. The thermometer is suspended in such a manner that the bulb may occupy as nearly as possible the centre of the fatty mass. The thermometer should be protected from currents of air, and should be kept perfectly still. The position of the mercury in the thermometer is carefully watched by the attendant as it gradually sinks toward the crystallising-point. When the crystals of the acid begin to appear in the bottom and on the sides of the test-tube, the descent of the mercury will become very slow and finally cease. The lowest point reached by the mercury should be noted. As the crystallisation extends inward towards the bulb of the thermometer a point will be reached when the mercury will begin to rise. At that point, the test-tube being held by the left hand, the thermometer should be taken by the right hand of the operator, and the partially crystallised mass of fat thoroughly stirred by turning the thermometer

three or four times around the tube in both directions. Care should be exercised that at the end of this operation the bulb of the thermometer should hang as near as possible in the centre of the crystallising mass. Directly the above operation is accomplished the mercury will be seen to rise, and this rise of temperature will continue for some time, after which the mercury will remain stationary

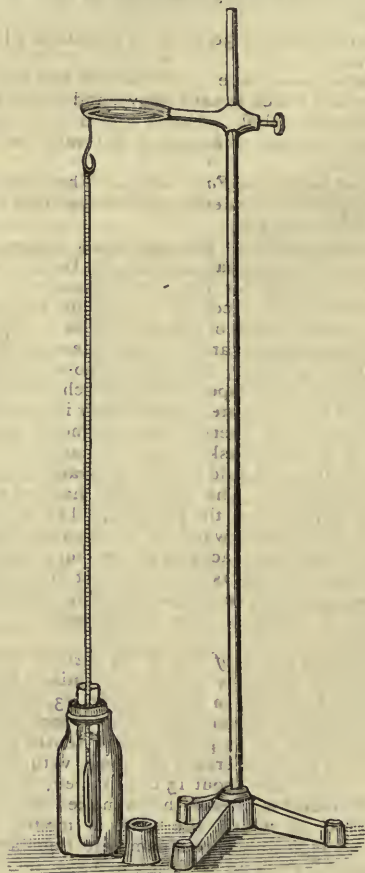


FIG. 5.

for one or two minutes. The highest point reached is taken as the true temperature of crystallisation.

Refractive Index.—The refractive index is conveniently determined by the apparatus of Professor Abbe, Fig. 6. The manipulation is conducted as follows:—Fine tissue paper or rather heavy body is cut into rectangular pieces 3 c.m. in length by 1.5 c.m. in breadth. One of these pieces of paper is placed on the lower of the two glass prisms of the apparatus. Two or three drops of the oil or fat are placed upon the paper and the upper prism carefully placed in position so as not to move the paper from its place. In charging the apparatus with the oil in this way, it is placed in the horizontal position. After the paper disc holding the fat is secured by replacing the upper prism, the apparatus is placed in its normal position and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus is now turned until the rainbow colours on the part between the dark and light field have disappeared. Before doing this, however, the telescope, the eyepiece of the apparatus, is so adjusted as to bring the cross lines of the field of vision distinctly into focus. The index of the apparatus is now moved back and forth until the dark

edge of the field of vision falls exactly in the intersection of the cross lines. The refractive index of the fat under examination is then read directly upon the scale by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus should be turned through an angle of 180° until the colours have again disappeared, and the scale of the instrument again read. These two readings should fall closely together, and their mean is the true reading of the fat under examination.

For butter fats the apparatus should be kept in a warm place, the temperature of which does not fall below 30°C . For reducing the results obtained to a standard temperature, say 25°C ., the following factor may be used. The

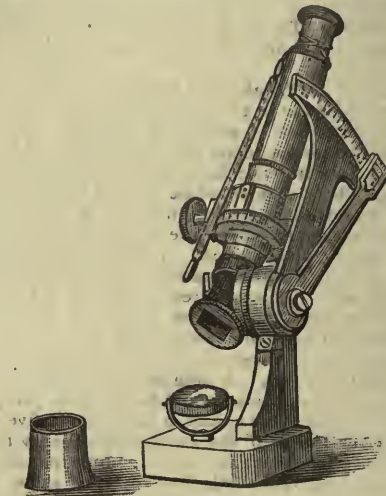


FIG. 6.

mean rate of variation in the refractive index of butter fats for each degree of temperature was determined by me in twelve samples of butter fat (see *Journal of Analytical Chemistry*, ii., Part 3, July, 1888). This factor is 0.000176. As the temperature rises the refractive index falls.

Example.

Refractive index of a butter fat determined at 32° $= 1.4540$, reduced to 25°C ., as follows:— $32.4 - 25 = 7.4 = 0.0013$; then $1.4540 + 0.0013 = 1.4553$.

The instrument used should be set with distilled water at 25°C ., the theoretical refractive index of water at that temperature being 1.3330. In the determination above given the refractive index of pure water measured 1.3300; hence the above numbers should be corrected for theory by the addition of 0.0030, making the corrected index of the butter fat mentioned at the temperature given, 1.4583.

Soluble and Insoluble Acids.—Use method described in *Bulletin 13*, Part 4, pages 455 to 461.

Saponification Equivalent.—Use method described in *Bulletin 13*, Part 4, pages 461, 462.

Rise of Temperature with Sulphuric Acid.—Use method described in *Bulletin 13*, Part 4, pages 443 to 446.

Decomposition of Ammoniacal Phosphorus Pentachloride by Heat. Phosphorus Chloronitride and Phospham.—A. Besson.—In 1890 the author indicated the existence of a compound $\text{PCl}_2\text{N}_3\text{H}_3$. If this substance is gently heated it loses ammonia. By the action of heat we obtain a chloronitride, $(\text{PCl}_2\text{N})_3$, and finally a greyish white solid body, phospham, PN_2H . Under the continued action of heat the phospham is gradually destroyed, with loss of nitrogen and hydrogen.—*Comptes Rendus*, cxiv., No. 22.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 282).

The Cause of the Deficiency.

It was by no means easy to trace the cause of the disappearance of less than one two-thousandth part of the material to its true source.

The notable agreement between the percentages of water given in the first three columns of figures immediately above of course suggested the possibility of a loss of copper and sulphuric acid during the electrolysis; and it became an important matter to test the point.

Accordingly weighed portions of a dilute solution of pure sulphuric acid were estimated with weighed amounts of sodic carbonate. Other portions of the same solution, weighed alternately with the previous ones, were then evaporated over the water-bath with small amounts of cupric nitrate and successive additions of water. The cupric sulphate formed by this treatment was wholly decomposed by electrolysis, and the resulting sulphuric acid was determined exactly in the usual manner. The comparison of the acid solution before and after electrolysis is capable of showing at once whether any sulphuric acid was mechanically or chemically lost during the process. If any nitric acid had been held by the sulphuric acid in the second case, it could not have escaped decomposition during the electrolysis.

Following are the results:—

Strength of H_2SO_4 before Electrolysis.

(Weights reduced to vacuum.)

No. of Exp.	Solution taken. Gms.	Na_2CO_3 required. Gms.	Na_2CO_3 for 10'000 grms. solution. Gms.
11.	5'5932	1'0175	1'81917
12.	11'4175	2'0768	1'81896
Average			1'81906

Strength of H_2SO_4 after Electrolysis.

(Weights reduced to vacuum.)

13.	16'8214	3'0592	1'81865
14.	5'5612	1'0115	1'81886
Average			1'81876

Difference between averages 0'0003.

Known mishaps tended to make the first experiments of each of the two groups respectively too high and too low. It is seen that the second experiments gave nearly identical results. Considering the increased transference and manipulation involved in the second group, the conclusion seems to be warranted that little, if any, sulphuric acid is lost during electrolysis.

In order to prove like relations with regard to copper a similar method was adopted. Weighed amounts of electrolytic copper were dissolved in pure nitric acid in a flask provided with bulb tubes for the condensation of spray. The cupric nitrate was then evaporated with an excess of sulphuric acid upon the water-bath, and the cupric sulphate was electrolysed as usual.

Electrolysis of Copper.

No. of Ex.	Copper taken. Gms.	Copper found. Gms.	Loss of Metal. Gms.
15.	1'24156	1'24139	0'00017
16.	1'00613	1'00600	0'00013

Here again, the manipulation was so much more elaborate than in a simple electrolysis that it is difficult to decide where the slight loss took place. In another experiment (No. 17) both copper and sulphuric acid were weighed before and afterward, but the experimental operations were so doubly involved that the determination was of very doubtful value. The result was not materially different from the others, however. The significant portions of the data will be given later on.

In the course of these experiments it was found that a compact and brilliant copper film may be safely washed by decantation if sulphuric acid alone is present. Indeed, during most of the preceding determinations this method was adopted to insure complete collection of the acid, and in only one case (experiment 7) was as much as one twentieth of a m.grm. of copper found in the filtrate. In this case that amount was added to the larger quantity, and the sum is given in the table. Potassic ferrocyanide was the reagent used in the colorimetric tests.

Assuming the deficiency of copper and acid as found above to represent a real loss during electrolysis, the composition of cupric sulphate would be:—

	Uncorrected.	Corrected.
Water	36'067	36'067
Copper	25'449	25'452
SO_4	38'435	38'442
	99'951	99'961

That is to say, an undoubtedly excessive value for this correction would account for only one-fifth of the deficiency for which explanation was sought. The correction is at best very doubtful, and it is not applied in the final calculation of the atomic weight. Its application would make no essential difference in the final result, but would render the individual variations much less marked.

The only probable interpretation of the deficiency now lay in the assumption that cupric sulphate still held a volatile impurity at 360°. Such an amount of any non-volatile foreign substance would have increased the weight of sodic sulphate found at the conclusion of the analysis by about eight one-hundredths of one per cent, an amount entirely too large to escape detection. Besides, such a source of error has already been shown to be unlikely.

After it had been experimentally proved that cupric sulphate had no tendency to hold ammoniac sulphate at 370°, the hypothesis of the occlusion of a small amount of water became the last resource. At first sight it seems improbable that any material could hold appreciable quantities of water in the presence of sulphuric acid when so strongly heated. But it must be remembered that at this temperature the acid is dissociated, and water is actually present in the vapour. It was hoped that sulphur trioxide might be more efficient as a dehydrating agent but a single experiment (No. 18) showed that cupric sulphate possessed more affinity for water, even at 300°, than did the sulphur trioxide. 2'3787 grms. (in vacuum), of cupric sulphate lost 0'8554 gm. in weight on heating to about 300° in a glass tube under a current of dry air. Upon continuing the application of heat in air charged with sulphuric anhydride from Nordhausen acid, no essential change in weight was observed. The apparatus was somewhat complicated in order to avoid rubber connections, but a description of it is superfluous. The total loss was 35'962 per cent of the weight taken.

Experiments showed that between 360° and 400° cupric sulphate does not essentially lose in weight. For example (No. 19 or 23), 1'28563 grms. of the substance dried at the former temperature weighed 1'28558 grms. after heating for ten hours at 400°. At the temperature of dull redness the salt slowly decomposes.

(To be continued).

* Contributions from the Chemical Laboratory of Harvard College, From the *Proceedings of the American Academy of Arts and Sciences*. vol. xxvi.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 19th, 1892.

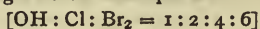
(Concluded from p. 286).

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

*19. "Studies on Isomeric Change. No. IV. Halogen Derivatives of Quinone." Part I. By ARTHUR R. LING.

Dichlorobromophenol [$\text{OH} : \text{Cl}_2 : \text{Br} = 1 : 2 : 6 : 4$], prepared from parabromophenol and sulphuryl chloride, crystallises from light petroleum in silky needles melting at 66.5° ; it gives metadichloroquinone when treated cold with nitric acid (1.5), and a mixture of dichloroparanitrophenol (m. p. 125°) and chlororthoparadinitrophenol (m. p. $110-111^\circ$) when warmed with nitric acid in glacial acetic acid solution.

Metachlorobromoquinone [$\text{O}_2 : \text{Cl} : \text{Br} = 1 : 4 : 2 : 6$], prepared by adding chlorodibromophenol—



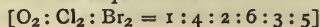
to cooled nitric acid (1.5), crystallises from alcohol in yellow needles melting at $114-115^\circ$. The quinol melts at $154-155^\circ$.

Paradichlorobromoquinone [$\text{O}_2 : \text{Cl}_2 : \text{Br} = 1 : 4 : 2 : 5 : 6$], obtained by brominating paradichloroquinone (m. p. 161°), melts at $160-161^\circ$. The quinol crystallises from water in monohydrated needles melting at $124-126^\circ$; the anhydrous substance melts at 135.5° . The diacetyl derivative melts at $158-159^\circ$.

Metadibromochloroquinone [$\text{O}_2 : \text{Cl}_2 : \text{Br} = 1 : 4 : 2 : 6 : 5$], produced by brominating metadichloroquinone (m. p. 121°), melts at 168° . The quinol crystallises from water in anhydrous needles melting at 135° , its diacetyl derivative melting at $173-174^\circ$.

Paradichloroquinone does not yield metadichlorodibromoquinone on bromination, as stated by Hantzsch and Schniter, but the normal product—paradichlorodibromoquinone—is obtained. *Paradichlorodibromoquinone* [$\text{O}_2 : \text{Cl}_2 : \text{Br}_2 = 1 : 4 : 2 : 6 : 3 : 5$], produced in this way, forms six-sided plates melting at 292° ; the quinol melts at $235-236^\circ$, its diacetyl derivative melting at $269-270^\circ$. The quinone does not yield chlorobromanilic acid on treatment with alkali, as Levy has stated, but a compound consisting of 1 mol. proportion of chloranilate and 2 mol. proportions of bromanilate. It is then shown that metadichloroquinone yields paradichlorodibromoquinone, identical in all respects with the last mentioned, when it is brominated in boiling glacial acetic acid solution; when, however, the bromination is conducted at the ordinary temperature, the product consists chiefly of the normal product, metadichlorodibromoquinone.

Metadichlorodibromoquinone—



is obtained exclusively when metadichlorobromoquinol (m. p. 135°) is suspended in carbon tetrachloride and heated in a closed bottle in a bath of boiling water, and the product oxidised; it crystallises from benzene in six-sided plates melting at 291° ; the corresponding quinol melts at $231-232^\circ$, its diacetyl derivative melting at $265-266^\circ$. The quinone yields chlorobromanilic acid on heating it with alkali.

*20. "Halogen Derivatives of Quinone." Part II. By ARTHUR R. LING and JULIAN L. BAKER.

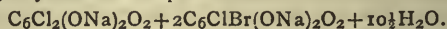
Chlorotribromoquinone, prepared by brominating monochloroquinol in acetic acid solution, and subsequently oxidising, crystallises from benzene in yellow, six-sided plates, and melts at 292° .

The formation of chlorobromanilic acid on treatment with alkali, as previously stated by one of the authors, was only observed in one experiment; in all others the molecular compound,—



was obtained. Chlorotribromoquinol crystallises from benzene in small colourless needles melting at $233-234^\circ$; the diacetyl derivative separates from benzene in needles melting at 275° .

Trichlorobromoquinone is obtained by brominating trichloroquinone; it separates from benzene in yellow six-sided plates and melts at $289-290^\circ$. On treatment with soda, it yields the compound—



The formation of chlorobromanilic acid, as stated by Levy and Schultz, was not observed. Trichlorobromoquinol, prepared by reducing the quinone, crystallises from benzene in flat needles melting at $230-231^\circ$, its diacetyl derivative crystallising from acetic acid in colourless needles melting at $261-262^\circ$. The authors draw attention to the fact that in the interaction of the tetrahalogen quinone and alkali at least 3 mols. of the quinone appear to be simultaneously concerned (compare also preceding abstract).

*21. "The Crystalline Forms of the Sodium Derivatives of Substituted Anilic Acids." By WILLIAM J. POPE.

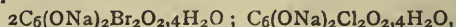
A comparison of the crystallographic dimensions of the sodium of the brominated and chlorinated anilic acids referred to in the preceding abstracts shows that the crystals possess considerable similarity. The salts examined crystallise in the anorthic system and have the following axial relations:—

Sodium bromanilate, $\text{C}_6(\text{ONa})_2\text{Br}_2\text{O}_{2.4}\text{H}_2\text{O}$, $a : b : c = 0.8768 : 1 : 0.8100$; $\alpha = 69^\circ 28'$; $\beta = 87^\circ 56'$; $\gamma = 71^\circ 49'$.

Sodium chloranilate, $\text{C}_6(\text{ONa})_2\text{Cl}_2\text{O}_{2.4}\text{H}_2\text{O}$, $a : b : c = 0.8743 : 1 : ?$; $\alpha = 88^\circ 8'$; $\beta = 89^\circ 51'$; $\gamma = 72^\circ 30'$.

Sodium chlorobromanilate, $\text{C}_6(\text{ONa})_2\text{ClBrO}_{2.4}\text{H}_2\text{O}$, $a : b : c = 0.888 : 1 : 0.814$; $\alpha = 69^\circ 59'$; $\beta = 87^\circ 3'$; $\gamma = 71^\circ 58'$.

A double salt, composed of 2 mol. proportions of sodium bromanilate and 1 of sodium chloranilate, having the composition—



is obtained by the action of caustic soda on paradichlorodibromoquinone and crystallises in the anorthic system. It possesses the constants $a : b : c = 0.8825 : 1 : 0.8163$; $\alpha = 69^\circ 48'$; $\beta = 87^\circ 14'$; $\gamma = 72^\circ 11'$. The same double salt, prepared by simply crystallising a mixture of the two constituents in the requisite proportions, gives numbers practically the same as these:— $a : b : c = 0.8825 : 1 : 0.8143$; $\alpha = 69^\circ 56'$; $\beta = 87^\circ 7'$; $\gamma = 72^\circ 11'$. The identity of the two samples of double salt prepared in different ways is thus established. The crystals of the above substances consist of small distorted prisms exhibiting the forms $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{1\bar{1}0\}$, and $m\{101\}$. The form $m\{101\}$ is not met with on crystals of sodium chloranilate, so that the axial ratio $b : c$ is in this case indeterminate. It is to be remarked that the chloranilate differs considerably in angular dimensions from the salts containing bromine, which approximate very closely to one another in geometrical properties. The crystals of these salts nearly always show a curious step-like structure, which extends in the direction of the c axis and frequently obliterates the forms $m\{101\}$ and $c\{001\}$ at the end of the crystal. A noteworthy fact is the great resemblance between the simple salts and the double salt of sodium brom- and chlor-anilate. The crystals of all the above-mentioned substances are, under ordinary conditions, opaque, but, when crushed to powder and examined microscopically, are seen to transmit light of a claret colour.

22. "Formation of a Hydrocarbon, $\text{C}_{18}\text{H}_{12}$, from Phenylpropionic Acid." By F. STANLEY KIPPING, Ph.D., D.Sc.

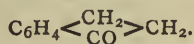
Having studied the action of phosphoric anhydride on a number of fatty acids (*Chem. Soc. Trans.*, 1890, 532, 980), it appeared desirable to ascertain whether benzenoid

acids would yield ketones under similar conditions; phenylpropionic acid was chosen. When this acid is heated with phosphoric anhydride, a reddish brown resinous mass is obtained; from this product I have so far succeeded in isolating three compounds, but others are doubtless formed.

1. A hydrocarbon, which after re-crystallisation from boiling xylene, gave on analysis results corresponding to the formula C_8H_{12} , 0.1515 grm. substance yielding 0.5250 grm. $CO_2 = 94.51$ per cent carbon, and 0.0710 grm. $H_2O = 5.21$ per cent hydrogen; the calculated values are carbon 94.74, hydrogen 5.26 per cent.

The hydrocarbon crystallises in pale yellow plates, does not melt at 250° , and is insoluble in most ordinary solvents, and only very sparingly soluble in boiling xylene; it is evident from its properties that it has a high molecular weight, its molecular formula being probably $C_{18}H_{12}$. It dissolves in hot, concentrated sulphuric acid, yielding a sulphonic acid which is readily soluble in water. On prolonged boiling with a mixture of potassium bichromate and sulphuric acid the hydrocarbon is converted into a deep yellow or orange compound; this substance is doubtless a quinone of the composition $C_{18}H_{10}O_2$, but as it is insoluble in all the ordinary solvents, and only very sparingly soluble in such liquids as boiling xylene, &c., it is not easily obtained in a pure condition; analyses gave about 1 per cent of carbon too much, probably owing to the presence of unchanged hydrocarbon. A dibromo-derivative of the composition $C_{18}H_{10}Br_2$ is formed when the hydrocarbon is treated with bromine; this substance crystallises from boiling xylene in microscopic needles, and does not melt at 300° .

2. The second compound which is formed by the interaction of phosphoric anhydride and phenylpropionic acid is of greater interest than the hydrocarbon; it is, however, produced in such small quantities that up to the present I have only obtained its hydrazone in a pure condition. This hydrazone crystallises from dilute alcohol in yellow needles, melts at $127-128^\circ$ with decomposition, and on analysis gives results agreeing well with those required by a compound of the composition $C_{15}H_{14}N_2$; when heated with concentrated hydrochloric acid it is converted into a colourless, crystalline compound, which melts at about 245° , is insoluble in water, and contains nitrogen. The constitution of the ketone (or aldehyde) from which this hydrazone is derived is, of course, at present quite a matter of speculation, but is possibly represented by the formula—



This view is supported by the fact that, by treating phenylpropionic acid with phosphorus pentachloride in order to convert it into the chloride $CH_2Ph \cdot CH_2 \cdot COCl$, and then warming an ethereal solution of this chloride with aluminium chloride, I obtained an oil which is insoluble in sodium carbonate, and which gives with phenylhydrazine a hydrazone identical with that described above.

3. The third product obtained by the action of phosphoric anhydride on phenylpropionic acid seems to be an organic derivative of phosphoric acid.

The experiments here described are still very incomplete, but it appears desirable to call attention to them as, if ketohydrindene derivatives are really produced in this way, their investigation cannot fail to be of interest.

23. "Metallic Derivatives of Acetylene." By R. T. PLIMPTON, Ph.D.

A report in the CHEMICAL NEWS (lxv., 169) of a preliminary paper read by Dr. Kaiser before the Chemical Section of the Franklin Institute, on the copper and silver compounds of acetylene, leads me to publish some of the results of an investigation of these and other metallic derivatives with which I have been engaged for some time past.

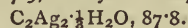
I.—Silver Compounds.

Silver Nitrate and Ammonia.—The precipitate formed by acetylene in ammoniacal silver nitrate is in dilute solutions (decinormal) bright yellow; in strong solutions the yellow, curdy substance first thrown down is prone to pass into a white and less bulky form. The yellow substance often undergoes the same change when allowed to stand under water containing acetylene and protected from light. The white substance usually yields a somewhat higher percentage of silver. Strong ammonia appears to be without action on the yellow acetylides, and the quantity present during precipitation does not influence the composition of the precipitate.

Silver estimations in eight specimens dried over sulphuric acid gave percentages of silver ranging from 87.38 to 88.85. Of these two had been tried for three and six weeks respectively, and yielded 88.7 and 88.8. Blockmann's formula $C_2Ag_2 \cdot H_2O$ requires 83.7; that of Berthelot, $C_2Ag_2 \cdot \frac{1}{2}H_2O$ or $(C_2HAg_2)_2O$, 86.7.

An attempt to prepare silver acetylides in neutral or acid solution, so as to diminish the risk of the precipitate carrying down with it silver oxide, was successful. Silver acetate is completely precipitated by acetylene with separation of the whole of the acetic acid. The acetylides so prepared has the same properties as that obtained in ammoniacal solution, but has not the same tendency to turn brownish on drying; and, like the latter, separates as a yellow, curdy precipitate, but may become white under the same conditions.

The silver was estimated in fifteen specimens carefully dried in a vacuum over sulphuric acid until they ceased to lose weight, and in some cases at $60-70^\circ$. The results lay between 86.6, the percentage of silver required for $C_2Ag_2 \cdot \frac{1}{2}H_2O$, and 87.9, nearly that required for—



Drying at $60-70^\circ$ caused a slight loss of weight, but caused the precipitates to darken. Those specimens which had become white yielded higher results than those which remained yellow. Two portions of the same precipitate, of which the one was left in contact with strong ammonia for several days, were dried, and yielded the same percentage of silver, 86.56.

The acetylene given off from a known weight of the dry substance with chlorhydric acid was measured and the silver chloride weighed; ratio of silver to acetylene, as 38 to 20 or 10.3 per cent carbon, $C_2Ag_2 \cdot \frac{1}{2}H_2O$, 9.7. Percentage of silver, 87.47. Other experiments by the same method, made with acetylides from ammoniacal silver nitrate and from silver acetate, also gave 1 mol. of acetylene to 2 atoms of silver.

Silver chloride dissolved in ammonia gave a yellow acetylides containing 87.85 per cent silver, and free from silver chloride.

Silver nitrate, in aqueous solution (decinormal), is precipitated by acetylene, three-fourths of the acid being liberated. Precipitates prepared from solutions of different strengths contained varying proportions of silver nitrate.

Alcoholic silver nitrate yields a precipitate much richer in nitrate, containing equal amounts of silver as acetylides and as nitrate. The action of hydrocarbons of the acetylene series on alcoholic silver nitrate has been studied by Behal. My analyses of precipitates from the nitrate gave as limits $3C_2Ag_2 \cdot 2AgNO_3Aq$ and $C_2Ag_2 \cdot 2AgNO_3Aq$, the latter being obtained from alcoholic solutions.

Silver sulphate solutions are also completely precipitated by acetylene, and with a solution containing 0.2 grm. in 100 c.c. two-thirds of the sulphuric acid was set free. Precipitates obtained from such a solution give results corresponding to $2C_2Ag_2 \cdot Ag_2SO_4Aq$.

II.—Mercury Compounds.

Mercuric acetate solutions yield white precipitates which become grey towards the end of the precipitation. If the solutions are not too strong the whole of the metal is thrown down with separation of all the acetic acid.

When washed with alcohol and dried *in vacuo* over sulphuric acid the substance has the composition required by the formula $3\text{HgO}_2\text{C}_2\text{H}_2$. It resembles the compound $3\text{HgO}_2\text{C}_3\text{H}_3\text{HgCl}_2$, obtained by Kutcheroff (*Ber.*, xvii., 13), from allylene, for, unlike the acetylides generally, it does not give off acetylene on treatment with chlorhydric acid, and is not explosive.

Iodine attacks it, apparently with formation of iodoform.

Mercurous acetate freshly precipitated and suspended in water is decomposed by acetylene and is converted into a greyish substance which differs entirely from the mercuric compound, and seems to be similar to silver acetylides in composition and properties. It detonates when heated suddenly, and gives acetylene on treatment with chlorhydric acid. Iodine acts upon it in the same way as upon silver acetylides, yielding di-iodoacetylene.

The acetylene used was prepared from the copper compound obtained from the incomplete combustion of coal gas, and was purified by caustic soda.

I propose to continue the study of the mercurous compound and the action of iodine on this and other acetylides.

24. "Isomerism amongst the Substituted Thioureas." By AUGUSTUS E. DIXON, M.D.

The author notes that, while it has been established that the addition product of a thiocarbimide XNCS with a primary amine YNH_2 is identical with that resulting from the combination of the thiocarbimide YNCS with the amine XNH_2 , no investigation appears, as yet, to have been conducted with the object of determining whether identical or isomeric forms would result if the substituting groups are similarly transposed in thiocarbimide and secondary amine.

In a communication recently made to the Society (*C. S. Trans.*, 1891, 551), two isomeric forms of methylphenylbenzylthiourea were incidentally described, but it was left undecided whether two ethylphenylbenzyl compounds resulting from the action of ethylthiocarbimide on benzylaniline, and of benzylthiocarbimide on ethylaniline, respectively, were identical or isomeric. Their isomerism has since been established by the observation that when heated with alcoholic ammonia, under pressure, the former yields ethylthiourea and benzylaniline, the latter benzylthiourea and ethylaniline. Furthermore, a third isomer is now described, produced from phenylthiocarbimide and ethylbenzylamine; this occurs in vitreous prisms insoluble in cold water, freely soluble in hot alcohol, chloroform, benzene, and carbon disulphide, and melting at $94-95^\circ$.

An isomer of Gebhardt's (*Ber.*, xvii., 3037) dimethylphenylthiourea (m. p. 114° , from MeNCS and MeNHPh) was also obtained, by the interaction of PhNCS and Me_2NH . It forms long white prisms, melting, without decomposition, at $134-135^\circ$. It is moderately soluble in boiling water, very freely in hot alcohol, and when boiled with aniline yields dimethylamine and thiocarbaniide.

25. "Note on Diastatic Action." By E. R. MORITZ and T. A. GLENDINNING.

It has been observed by one of the authors that brewers' worts, as they issue from the mash tun, remain constant in respect to their starch transformation products when digested for two hours at the same temperature as that at which the conversion was conducted. The diastase in these solutions therefore exercises within such a period no action on the starch products contained in it; but if fresh starch be added, the residual diastase is found yet to possess considerable power of liquefying and saccharifying starch, although its energy is distinctly inferior to that of the original malt. The authors describe a series of experiments made with the object of comparing the energy of the original with that of the residual diastase.

They consider that the results entitle them to form the following conclusions:—

The attainment of a resting stage in the transformation of starch by diastase by no means shows that the energy of

the diastase is exhausted. The energy of the "residual" diastase is, in fact, very considerable, even under conditions adverse to its activity. It is somewhat weakened by increasing the amount of starch it has to convert, but it is weakened to a marked extent by subjecting it for some time to a temperature exceeding the optimum one for saccharification. When, however, it is not exposed for any length of time, whether previous to the first or to subsequent transformations, to a temperature exceeding the optimum, it appears capable, after transforming a considerable amount of starch, to transform further quantities to nearly the same point, when such further quantities are added successively and subsequent to the attainment of the resting stage in the preceding transformation.

PHYSICAL SOCIETY.

Ordinary Meeting, May 27th, 1892.

MR. WALTER BAILY, M.A., Vice-President, in the Chair.

THE following communication was read "On the Present State of our Knowledge of the Connection between Ether and Matter: an Historical Summary," by Prof. O. J. LODGE, F.R.S.

Referring to difficulties connected with the aberration of light, if the medium were supposed to be carried along by the earth in its orbit, Dr. LODGE described Boscovich's suggested experiment with a telescope filled with water, carried out by Klinkerfues, who was led to conclude that the "aberration constant" depended on the medium within the telescope. Klinkerfues' experiments were repeated by Sir G. B. Airy, but not confirmed. Astronomical observations were not necessary to determine the point at issue, for a fixed source near a collimator might be used with advantage. Hoek has examined the subject in this way with similar negative results. It might therefore be concluded that surveying operations are unaffected by terrestrial motion. This result, however, did not prove the existence or non-existence of an ether drift relative to the earth, for since the source and receiver move together any effect produced by such a drift would be compensated by aberration due to motion of the receiver.

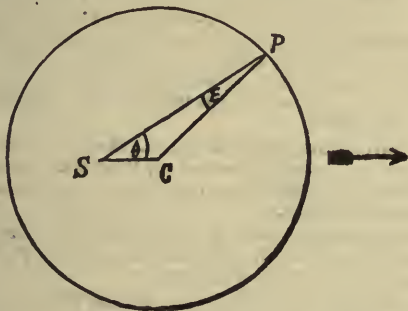
Speaking of refraction, he pointed out that if the ether were stationary in space, glass and other terrestrial bodies would have ether streaming through them, and that the refraction of say, glass, might differ as the direction of the ether drift through it varied. To test this Arago placed an achromatic prism over the object glass of a telescope on a mural circle, and observed the altitude of stars. To vary the direction of the ether drift through the prism, stars in different azimuths were observed, but the results showed no appreciable change in the deviation produced by the prism due to direction of the earth's motion. Maxwell used a spectroscope to test the same point. Light from illuminated cross wires passed through the telescope, prisms, and collimator, and was reflected back along the same path by a mirror and viewed through the telescope. Observations made with different aspects of instrument showed no change in the relative positions of the wires and their images.

Mascart had also tried the experiment with simpler apparatus, but was unable to detect any change.

These observations naturally suggest that the ether is at rest relative to the earth, but the apparently simple nature of aberration makes this view difficult to hold. Both phenomena are consistent with Fresnel's hypothesis, that only the excess of ether which the substance possesses over that of surrounding space moves with the body; for on this supposition the effects of altered refraction and ether drift compensate each other. Fresnel's view is practically established by Fizeau's well-known experiment on the effect of moving water on the velocity of light, and by the more accurate numerical results

obtained by Michelson. The only other theory which accounts for the experimental results is one by Prof. J. J. Thomson, which requires that the velocity of light in Fizeau's experiment should be altered by half the velocity of the medium. For media whose refractive indices are $\sqrt{2}$, the two theories lead to the same result, and as the indices of substances such as water do not differ much from this value, it is difficult to discriminate between them.

Looked at in another way Fizeau's experiment raises a difficulty; for, as Dr. LODGE pointed out, all water is moving with the earth, hence light should be hurried or hindered, according to the direction in which it passes through the water. This effect doubtless exists, but the results of it have never been detected by experiment. It is therefore necessary to inquire why the effect could not be observed directly, for the experiment had been tried with interference apparatus by Babinet, Hoek, Jamin, and Mascart, and in no case was any effect observed. It would therefore seem as if the ether must be stagnant, *i.e.*, stationary relative to the earth. Mascart had also tested whether Newton's rings or the rotatory power of quartz were affected by ether drift, but with negative results. These observations are, however, likewise compatible with Fresnel's hypothesis of an ether fixed relative to matter, and a free ether of space permeating all sub-



stances, for, according to this view, there is no more motion of the ether in water or glass than in air; hence the time of journey round a closed contour is independent of the direction in which the light traverses that contour. The time of journey between two points is also unaffected by terrestrial motion, as was proved by the experiments of Babinet, Hoek, and Mascart, on interference; hence he (Dr. LODGE) inferred that ether was either stagnant or had a velocity potential.

In moving ether it was necessary to define a ray, and Lorentz's method is the best. Suppose CP represents the velocity of light (V) in still ether, and SC the velocity of the ether (v), then a disturbance originating at S will travel along SP, which is the direction of the ray, whilst CP is the wave normal. In the above figure—

$$\frac{\sin \epsilon}{\sin \theta} = \frac{SC}{CP} = \frac{v}{V} = a,$$

the constant of aberration. The velocity along the path of the ray is SP. Calling this velocity V' we have, $V' = V \cos \epsilon + v \cos \theta$. The path of a ray is determined by the time of journey being a minimum, and the formula—

$$T = \int_A^B \frac{ds}{V} = \text{a minimum,}$$

is the equation to a ray, where A and B are the extremities, and ds an element of the path.

If the ether be moving, V' must be substituted for V , and we get—

$$T' = \int_A^B \frac{ds}{V' \cos \epsilon + v \cos \theta} = \text{a minimum.}$$

This integral can be written exactly—

$$T' = \int \frac{ds}{V} \frac{\cos \theta}{1 - a^2} - \int \frac{v \cos \theta}{V^2 (1 - a^2)} ds = \\ = \frac{T \cos \theta}{1 - a^2} - \int \frac{v}{V^2} \frac{\cos \theta}{1 - a^2} ds.$$

The last term is the only one involving the first power of ether drift, and it vanishes in case there is a velocity

potential; for since $v \cos \theta = \frac{d\phi}{ds}$, where ϕ is the velocity

potential, it may be written $\frac{\phi_B - \phi_A}{V^2 (1 - a^2)}$, and so its value

depends only on the end points, and not on the path. If these points are the same, *i.e.*, the contour is closed, it becomes zero, and reconciles all the experiments hitherto made. It must be admitted, however, that if a is not a constant the question is again opened, but there is no reason to suppose it can vary in the same horizontal plane.

If the medium be changed, V becomes $\frac{V}{\mu}$, and in order to retain the same velocity potential in the changed

medium, v must become $\frac{v}{\mu^2}$, which is Fresnel's law.

Hence Prof. LODGE pointed out that the velocity potential condition includes Fresnel's law as a special case.

It can, in general, be inferred that *no first order optical effect due to terrestrial motion can exist in a detectable form*. It is always compensated by something else. Quantities of the second order of magnitude must therefore be attended to. From the first equation above, it follows that $\cos \epsilon = \sqrt{1 - a^2} \sin^2 \theta$, and the time of journey in moving ether is given by—

$$T' = T \frac{\sqrt{1 - a^2 \sin^2 \theta}}{1 - a^2},$$

where T is the time if everything were stationary. This is, in brief, the theory of Michelson's recent experiment. If the light travels along the ether drift $\theta = 0$, and

$$T' = \frac{T}{1 - a^2},$$

whilst if $\theta = 90^\circ$,—

$$T' = \frac{T}{\sqrt{1 - a^2}}.$$

Therefore the velocity along the ether drift should differ from that across the drift in the ratio of $\sqrt{1 - a^2} : 1$. This point has been very carefully tested by Michelson, but nothing approaching to a quarter of the theoretical effect was observed. His negative result would seem to preclude any relative motion, even irrotational, and show that the ether is at rest relative to the earth's surface. On the other hand, the author (Dr. LODGE), has recently made experiments on the influence of rapidly rotating steel discs on the ether, which prove that the ether is not affected by the motion of contiguous matter to the extent of a 200th part of the velocity of the matter. These experiments are at present in conflict. Prof. Fitzgerald has suggested a way out of the difficulty by supposing the size of bodies to be a function of their velocity through the ether.

Returning to the statements which have been made of Fresnel's law, Glazebrook has shown that actual extra density of ether is not necessary, for if the virtual mass be altered, the same results follow; all that is required is a term depending on the relative acceleration of ether and matter. To modern ideas the loading of the ether by the presence of matter is most likely to be correct, and the observed effects of relative motion are regarded as the results of secondary reactions of matter on ether. On this

view the ether of space may be wholly unaffected by the motion of matter. On the vortex ring theory of matter, it is not unnatural to suppose that the ether in its neighbourhood should be only affected irrotationally by its motion. And if the velocity potential be granted, nothing of the nature of viscosity being admissible, the results of all the interference, refraction, and aberration experiments could be predicted, and the whole theory is as simple as it can possibly be. The only reliable experiment ever made which tends against this view is that of Michelson. The author surmised that this must somehow be explained away.

In reply to a question by Prof. Ayrton, Dr. LODGE said that when air was substituted for water in Fizeau's experiment, no effect is observed. This might have been expected, for the difference in the times of journey by the two paths depended on $\frac{\mu^2 - 1}{\mu^2}$, and as μ is nearly unity

for air, the air effect is too small to see.

(NOTE by Dr. O. J. LODGE.—In Hoek's interference experiment it might be said that ether moving in stationary water is balanced by that of the ether moving in stationary air; but while motion of water itself would disturb the balance, motion of air would do nothing appreciable. The only kind of motion that could display an optical effect is rotational motion, or motion of layers at different speeds, not a simple uniform drift.

Prof. J. V. Jones asked how the Fizeau experiment could be expressed on the loaded ether theory; for since the speed of matter affects the velocity of light, it seemed to involve a directional loading. A mere extra density term or acceleration coefficient will not explain this; it seems to require a coefficient of a velocity term. This question has been hinted at by Lord Rayleigh, who points out (under the heading "Aberration," *Nature*, March, 1892) that the rate of propagation of waves on a loaded string will be affected by a travelling of its load. The question is not perfectly simple, and the analogy not complete. A good deal depends on the nature of the connection symbolised as "loading)."

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY IN COURT.

To the Editor of the Chemical News.

SIR,—The Institute of Chemistry, a body which is endowed with a charter, has at length exercised its disciplinary powers and expelled one of its Fellows. But whilst maintaining its technical right to expel for unprofessional conduct, or for what it deems to be unprofessional conduct, it has in this instance awarded to its expelled Fellow a valuable testimonial in the shape of a declaration in the Queen's Bench Division of the High Court, that the expulsion "casts no imputation upon the professional capacity or personal character" of the expelled Fellow.

This seems very strange. We can easily understand that a Fellowship lapsing through inability or unwillingness to pay the annual subscription requisite to keep up the Fellowship, should not cast any imputation on the holder of the Fellowship. But that a deliberate expulsion from the Institute,—and an expulsion following upon a refusal to resign,—should cast no imputation, that is wonderful indeed.

The explanation is, however, supplied by the record of the proceedings in the case.

The cause of the expulsion was in this instance of a political character. The expelled Fellow, who had an objection to the assumption of the functions of Public Analyst by an alien, gave effect to his objection by making an application for an appointment of Public Analyst where there was an alien analyst.

Thereupon two events happened. The alien analyst took out letters of naturalisation and complied with the law, and at the same time complained to the Institute, which expelled its Fellow whose public spirited action had put a stop to a grievous scandal.

Hence the strange anomaly of expulsion from the Institute of Chemistry being accompanied by the bestowal of a valuable certificate of character and competence.

The Institute possesses arbitrary powers. Any one of its Fellows is liable to expulsion upon the most frivolous of pretences; but a frivolous expulsion brings in its train a certificate of character and competence which is at least as valuable as the Fellowship, and is certainly a more permanent possession.—I am, &c.,

J. ALFRED WANKLYN.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 22, May 30, 1892.

On Cadmium Hydrosilicate.—G. Rousseau and G. Tite.—The hydrosilicate, $2(\text{CdO}, \text{SiO}_2) \cdot 3\text{H}_2\text{O}$, is soluble in hydrochloric acid, with deposition of pulverulent silica. It loses little of its water at dull redness. Near orange redness it melts to a colourless transparent glass, and undergoes a loss of weight greater than that due to its total dehydration.

On Strontium Phosphate.—L. Barthe.—The author describes the neutral compound, PO_3SrO , the monacid compound, PO_3SrOH , and the diacid compound, $\text{PO}_3\text{SrO}, 2\text{HO} + 2\text{HO}$.

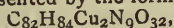
The Calorific Power of Coal, and Formulæ for its Determination.—M. Scheurer-Kestner.—This paper does not admit of useful abstraction.

Mechanical Determination of the Boiling-Points with Complex Terminal Substitution.—G. Hinrichs.—A purely mathematical paper.

Certain Reactions of the Three Amidobenzoic Acids.—Oechsner de Koninck.—If orthoamidobenzoic acid is heated with a small excess of pure potassium nitrite there is formed a colouring-matter which dissolves with a garnet-red colour in water containing a little alcohol. If meta- and para-amidobenzoic acids are similarly treated they form red colouring-matters soluble in dilute alcohol. If we treat the acids with a small excess of pure ammonium nitrate and heat gradually to fusion we see two strata, the lower light red and the upper violet. With a smaller proportion of the salt there is formed a dark red or brown colouration. If we allow the mixture to cool for a moment and then add a little water, the liquid is decolourised. On heating again it resumes its original colour. If we heat gently mixtures of uranium nitrate and of the three isomers, we find with the ortho-acid the formation of a bright red sublimate, whilst alcoholised water takes an amber yellow. With the meta-acid the sublimate is brown, and the alcoholic water takes a red-brown colour. With the para-acid the sublimate is orange, and the solution in alcoholic water is deep yellow. Chloride of lime was used as a paste. On mixing equal portions of this and of the ortho-acid there was formed a deep violet paste. When cold it was taken up in concentrated acid, giving a solution bright red by transmitted light, but reddish-brown by reflection. After some time there appeared a fine violet fluorescence. With the meta-acid the liquid was a solferino-red by transmitted, but bright red by reflected light; no fluorescence. The para-acid gave a deep red alcoholic solution not fluorescent. Mixtures were made up of equal parts

of granulated zinc chloride and the three isomers, and heated to the melting point of the latter. The ortho-acid gave an amber colour and dissolved in hot concentrated alcohol. The meta- and para-acids yielded a deep violet colour. Sometimes greenish reflections were observed. With stannous chloride heated progressively the mixture of ortho-acid and of a slight excess of the salt melted to a thick amber liquid. The meta-acid gave a yellowish white liquid, and the para-acid a bright yellow. Water and alcohol dissolved nothing in the cold. The ortho-acid, if heated gently with a slight excess of stannic chloride and allowed to cool, dissolved in alcoholised water with a solferino-red. The meta- and para-isomers gave no reaction.

The Composition of Chlorocruorine.—Dr. A. B. Griffiths.—This substance is a respiratory pigment, existing in two states, oxidised and reduced. The former presents two absorption bands, the one between C and D and the other between D and E. The reduced chlorocruorine has only one band between C and D, less definite. The author has determined the composition of this pigment as obtained from the blood of *Sabella*. The result leads to the complex formula $C_{560}H_{845}N_{143}FeS_3O_{167}$. According to Prof. Church, turacine, from the feathers of the turaco, is represented by the formula—



and presents some analogies with hæmatine.

The Antiseptic Properties of Formaldehyd.—A. Trillat.—One of the most remarkable properties of formic aldehyd is its sterilising property. Urine mixed with this liquid becomes incapable of putrefaction. Its sterilising power with broth containing *Bacillus anthracis* is still more marked than that of mercuric chloride.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Estimation of Cyanides.—Can any of the readers of the CHEM. NEWS inform enquirer where Dr. Kennblanch's method for the estimation of cyanides in spent oxide from gas-works can be found?—J. P.

Analytical Chemists as Jurymen.—Could any of the readers of the CHEMICAL NEWS inform me whether analytical chemists can claim exemption from serving as jurymen (common) at Assizes and Quarter Sessions, on the ground that they are professional men?—ANALYST.

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Photographic, 8.

WEDNESDAY, 22nd.—Geological, 8.

THURSDAY, 23rd.—Royal Society Club, 6.30. (Anniversary).

FRIDAY, 24th.—Physical, 5. "Breath Figures," by W. B. Croft.

"The Measurement of the Internal Resistance of Cells," by E. Wythe Smith. "Units of Measurement," by Mr. Williams.

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THE CHEMICAL NEWS.

VOL. LXV., No. 1700.

THE FLAME OF BURNING NITROGEN.

By W. CROOKES, F.R.S.

NITROGEN is a combustible gas; that is to say, a mixture of nitrogen and oxygen (atmospheric air) will under certain conditions burn with a flame, and production of nitrous and nitric acids. The reason why, when once nitrogen is set on fire, the flame does not spread throughout the whole atmosphere and deluge the world in a sea of nitric acid, is that the igniting-point of nitrogen is higher than the temperature produced by its combustion, and therefore the flame is not hot enough to set fire to the adjacent gas.

In the experiments shown at the Soirée of the Royal Society on June 15th, an electric current of 65 volts, and 15 ampères, alternating 130 times a second, was passed through the primary of a large induction coil, when an arching flame, consisting chiefly of burning nitrogen, issued from each of the secondary poles, meeting at the centre. When once started the poles can be drawn asunder till the flame bridges across 212 m.m. When the terminals are more than 46 m.m. apart, the flame will not strike across. When alight the flame is easily blown out by the breath, and it can then be re-lighted by a taper.

In the spectroscope the flame of nitrogen shows no lines, the spectrum being faint and continuous. The temperature is a little higher than that of a good blowpipe flame, easily melting fine platinum wire. The hot gases rising from a flame have a strong odour of nitrous acid, and when it is produced in a closed globe, the interior rapidly fills with red gases.

The flame produced by exciting an induction coil by means of an alternating current was first observed by Mr. Spottiswoode, F.R.S., who described it before the Royal Society in 1880. It has lately been exhibited on a magnificent scale at the Crystal Palace, by Messrs. Siemens Bros., and by Messrs. Swinburne and Co. It is not known, however, that any chemical explanation of the flame has before now been published.

NOTE ON THE ANALYSIS OF SLAG OF METALLIC APPEARANCE FROM THE MANUFACTURE OF PHOSPHORUS IN ELECTRICAL FURNACES.

By JOHN C. CHORLEY, F.C.S.,
University College, London.

THE process of manufacture in which this slag is formed may be briefly described as follows:—The materials, consisting of redonda phosphate (native phosphate of alumina), some form of calcium phosphate, carbon, and sand, are first heated in an auxiliary furnace and are then fed into the electrical furnace, built of firebrick, in the form of a rectangular trough. An alternating current of about 5000 ampères with an E.M.F. of 50–60 volts, is employed (*Journ. Soc. Chem. Ind.*, x., 5445). Owing to the intense local heat, most of the oxygen combines with the carbon present and phosphorus distils over. Two distinct kinds of slag are formed, that largest in quantity being chiefly silicate of lime and alumina, whilst the other, containing iron, silicon, and phosphorus, is distributed throughout the mass in more or less globular buttons. Three separate samples of this latter slag were obtained

at different tappings; all were steel-grey in colour, very hard and brittle, and breaking with a metallic fracture; it appeared quite homogeneous, but did not exhibit any crystalline form under the microscope. When examined in the state of very fine powder with a $\frac{1}{4}$ th objective, a few particles of transparent matter were observed, evidently silica. The slag is extremely stable; it is easily fusible with the oxyhydrogen blowpipe, a little oxidation taking place. Hydrochloric and nitric acids, dilute or concentrated at 100°, have little or no action upon it. After being heated to 100° with aqua regia for thirty hours very little action could be detected. With hydrofluoric acid it is practically unaltered.

With dilute sulphuric acid a similar result was obtained; but long boiling with concentrated sulphuric acid decomposes it partially.

Direct fusion in a platinum crucible is impossible, as the phosphorus at once attacks the platinum.

When heated in a current of sulphuretted hydrogen a superficial layer of sulphide of iron is formed.

There is very little action when it is heated with bromine or iodine.

Only two methods of decomposition were found available for analysis.

1. By heating the finely-powdered slag in a porcelain boat in a current of dry chlorine, and passing the gases first through water and then through a dry plug of cotton wool to retain solid particles, the iron was then volatilised as Fe_2Cl_6 , the silicon as SiCl_4 , which was decomposed by the wash water, and the phosphorus as PCl_5 or PCl_3 ; in about an hour complete decomposition was effected, only a little silica being left in the boat. The contents of the whole apparatus were then washed into a basin, and after the addition of hydrochloric acid evaporated to dryness and heated to render silica insoluble.

After adding weak hydrochloric acid the silica was filtered off and weighed; the filtrate was then evaporated several times to dryness with nitric acid in order to oxidise the phosphorus completely, and was finally dissolved in weak hydrochloric acid and diluted to 250 c.c. The iron in 25 c.c. was estimated by titration in sulphuric acid solution with permanganate of potash, and the phosphorus in 25 c.c. as $\text{Mg}_2\text{P}_2\text{O}_7$, with intermediate precipitation with ammonium nitro-molybdate, and in certain cases directly as ammonium phospho molybdate.

2. This method, in part new, was as follows:—(a) The finely-powdered slag was heated with excess of a neutral solution of copper sulphate in a sealed tube to about 170° for four to five hours. A considerable quantity of metallic copper was precipitated with some phosphide of copper, while some iron, phosphorus, and silicon went into solution; when the tube was opened there was no pressure. The contents were washed out and treated with sufficient nitric acid to dissolve the copper, and the residue was filtered off; the filtrate was then evaporated to dryness with hydrochloric acid and silica estimated. The copper in the filtrate was precipitated with hydrogen sulphide and the filtrate from this added to the similar filtrate in the second part of this method. (b) The residue from (a) was fused with about five times its weight of fusion mixture at a bright red heat for one hour in a platinum crucible, and when cold the contents were dissolved in dilute hydrochloric acid and evaporated to dryness, and silica estimated as usual. The filtrate was then mixed with the filtrate from (a) made up to 250 c.c., and the analysis was continued as in the first method.

The mean results obtained were as under:—

	Sample No. 1.	Sample No. 2.	Calculated for Fe_2PSi_2 .	Sample No. 3.	Calculated for Fe_2PSi_2 .
Fe	70.55	68.75	72.02	73.79	74.01
P	9.84	10.84	9.97	14.63	13.63
Si	17.90	19.10	18.00	10.31	12.33
O and loss ..	1.71	1.31	—	1.87	—

This slag may be a definite compound containing a small amount of impurity. The analysis of Nos. 1 and 2

agrees fairly well with the formula Fe_4PSi_2 , and that of No. 3 with Fe_3PSi . Or it may be a mixture of silicide and phosphide of iron in varying proportions. As it is not crystalline, the last view is perhaps the correct one; yet silicide of iron is easily attacked by acids, and this compound is not, and its power of resistance may be due to the existence of some definite compound.

The specific heat was determined and found to be 0.146, being very close to that calculated for a mixture of its constituents, viz., 0.142, the specific heat of iron being taken as 0.114, that of phosphorus as 0.174, and silicon as 0.173 (Regnault). The specific gravity was found to be 5.965. The substance is a conductor of electricity.

MOLYBDIC ACID AS A COLOUR REAGENT FOR CERTAIN AROMATIC OXY-COMPOUNDS.

By J. STAHL.

HÄGER some time ago indicated a reaction for the tannic acid of galls and other tannic acids, according to which these substances give fine reddish-yellow colours with ammonium molybdate. I have found that the same reactions occur for certain compounds approximating on tannin, pyrogallol, pyrogallo-carbonic acid, and gallic acid. As all four substances named contain oxy-groups in an ortho-position to each other, the reagent was tried also for other aromatic compounds in which the same case occurs. The result was that ammonium molybdate is a specific colour-reagent for all aromatic compounds which contain two or more oxy-groups standing in the ortho-position to each other.

Ammonium molybdate produces intense phenomena of colouration only with such bodies, which, according to the substance employed, may be yellow, reddish-brown, or blackish-brown. On the contrary, in all organic compounds in which the above mentioned condition does not occur no colouration is recognised. Thus, with pyrocatechin on the addition of the molybdate there is shown an intense reddish brown colour, which does not appear with hydroquinone and resorcin, a behaviour which shows phloroglucine in contrast to pyrogallol. The following aromatic compounds display similar colourations:—Protocatechuic acid, caffeic and hydrocaffeic acid, phenanthrenhydroquinone and retenehydroquinone; in alizarin, purpurin, anthragallol, and rufigalic acid, the aqueous solutions of which are yellow or red, the tone is much intensified by an addition of the molybdate. The entrance of other groups into the nucleus does not generally interfere; thus the reaction appears in the bromo- and nitro-derivatives of pyrogallol and gallic acid, but not in the phenol ethers, where one or more hydrogen atoms of the oxy-group are replaced by alkyls, as guaiacol and vanilline. Very slight yellow colourations which may occur with the two last mentioned bodies are probably due to slight impurities. Among compounds of a less fully known constitution the reaction is produced by quercitrin and its scission product quercetin, apomorphin, podophyllin, koussein, and aloin.

The aqueous solution of free molybdic acid behaves exactly like ammonium molybdate. The latter, in presence of organic substances, passes to a lower stage of oxidation, with the production of a blue, yellow, or a reddish-brown.

The origin of the colour phenomena in question depends on the oxidising action of molybdic acid and its ammonium salt. As those aromatic compounds which contain oxy-groups in the ortho-position to each other are more unstable and especially more readily oxidisable than their isomers, there occurs here a more energetic reduction of the molybdic compounds. The stage of the blue oxide is overleaped, and there appear at once the lower brownish stages of oxidation. If heat is applied

and the reaction is prolonged, brownish-black masses separate out which are found to be a variable mixture of lower molybdic acids, whilst a portion of the organic substance is oxidised to carbonic acid and water. But it is not impossible that there may appear simultaneously yellow or brown oxidation products of the oxy-compounds.

The sensitiveness of these reactions is not very great, but in case of pyrocatechin, pyrogallol, gallic acid, and tannin, it admits of the recognition of 0.1 m.grm. substance in 1 c.c. of liquid. The action of sodium tungstate is similar to that of ammonium molybdate.—*Ber. Deuts. Chem. Gesell.*

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 293).

If the loss of weight during this decomposition could be compared with the deficiency of sulphuric acid in the residue, it is evident that an indirect means would be at hand for the detection of a possible simultaneous loss of water. Such a circuitous road seemed to be the only one open to the present search.

In the series of experiments tabulated below, pure cupric sulphate was heated in the usual manner to 250°, and then after the addition of sulphuric acid to 400°, until the salt became constant in weight. The heat was then increased to dull redness, and after cooling the loss of weight was determined. Upon solution of the residue in water a small amount of basic salt was naturally deposited. Since the filtrate was apparently quite normal, it is evident that the amount of sulphuric acid necessary exactly to dissolve this precipitate must have been equivalent to the anhydride driven off.

After standing a considerable time, the basic salt was carefully filtered off and a measured amount of twentieth normal acid was used for its solution. The crucible used for the ignition was also washed with a measured quantity of acid. The clear solutions were all combined, and the excess of acid was determined by sodic hydroxide and methyl orange. Since the loss of weight upon ignition was noticeably more than the amount of anhydride corresponding to the quantity of sulphuric acid used to dissolve the basic salt, something besides sulphur trioxide must have been expelled by the heat.

The last column of the table gives the difference between the loss of weight of the cupric sulphate and the amount of sulphuric anhydride required to dissolve the basic salt, expressed in percentage of the original crystallised compound. This difference probably represents a small amount of water held even at 400°. The results showed a very noticeable variation, and at first sight appeared somewhat unsatisfactory. The first two experiments agreed well with each other, and were apparently very trustworthy. In the third, on the other hand, the amount of basic salt was so large as greatly to interfere with the accuracy of the result. In Experiment 23 the loss of weight upon ignition was so very large, amounting to about three per cent of the anhydrous sulphate, that the experiment was rejected. After such a failure it was natural that the next sample should not have been heated enough. This result is hence probably too low. The last experiment was more carefully regulated, and is more trustworthy. In this case the cupric sulphate was heated for an hour at very dull redness.

The filtrates from the precipitates of basic salt did not deposit any further solid upon long standing. That from the last determination was rendered very distinctly acid

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

Action of Heat upon Cupric Sulphate.

Weights reduced to vacuum.

Number of Expt.	Weight of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Grms.	Weight of CuSO_4 [260°]. Grms.	Weight of CuSO_4 [400°]. Grms.	Weight after ignition at dull redness. Grms.	Loss between 400° and redness. M.grms.	1·20 normal H_2SO_4 required for basic salt.		Per cent of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ unaccounted for.
						Uncorr. C.c.	Corr.* C.c.	
20.	—	1·5822	1·57945	1·57325	6·2	2·65	2·55*	0·044
21.	2·71828	1·7413	1·73836	1·73130	7·06	2·95	2·85*	0·050
22.	4·7325	—	3·0258	2·9928	33·0	16·36	[15·86*?]	[0·030?]
23.	2·01084	1·2880	1·2856	1·2504	35·2	—	—	—
24.	7·211	—	4·6075	4·6055	2·0	0·33	0·32*	0·019
25.	3·979	—	2·5443	2·5403	4·0	0·93	0·90*	0·055

Total average 0·040
Average omitting 22.. .. . 0·042

(* See Experiments 26—27).

to methyl orange by the addition of a milligram. of sulphuric acid, in spite of the difficulty in detecting the colour-change in the presence of the blue cupric sulphate. These tests indicate that the filtrate was wholly normal.

In order to test still more definitely the accuracy of the method the following mode of procedure was devised. To neutral solutions of cupric sulphate—prepared either from the purest crystals or by long standing after the neutralisation of the trace of acid in ordinary “chemically pure” material—were added small measured amounts of a standard sodic hydroxide solution. After a time the precipitate was filtered off and dissolved in standard sulphuric acid, exactly as if it had been obtained by the expulsion of the acid through heat.

Test of Method.—Precipitation and Solution of Basic Cupric Sulphate.

No. of experiment.	Concentration of solution.	Time between precipitation and filtration.	Twenty-second normal NaOH used. C.c.	Twenty-second normal H_2SO_4 used. C.c.	Factor $\frac{\text{c.c. NaOH}}{\text{c.c. H}_2\text{SO}_4}$
26.	Strong.	10 mins.	3·00	2·85	1·05
27.	Strong.	90 mins.	3·00	2·94	1·02
28.	Medium.	15 hours.	3·00	3·14	0·95
29.	Dilute.	1 hour.	6·00	6·24	0·96
30.	“	90 mins.	6·00	6·27	0·95
31.	“	“	3·00	3·12	0·96
32.	“	“	3·00	3·14	0·95
33.	“	“	3·00	3·03	0·99

Average of Experiments 28-33 0·96

It is hence evident that from dilute solutions the basic salt is wholly precipitated in a comparatively short time. Even under the worst conditions no deficiency approaching that noticed in Experiment 25 was observed. Another series (Experiments 34—37), made in very dilute solutions without filtering, gave values for the factor which respectively equalled 0·97, 0·98, 0·95, and 0·98. The average is 0·97, not seriously different from that found above. The first value of the factor was used in correcting the results of Experiments 20—25. The correction involved is extremely slight except in Experiment 22, where the application of the full value of the factor to a very large quantity is of doubtful advisability. Hence it is better to omit this experiment from the final average.

One contingency alone is not provided for by these test experiments; that is to say, the formation of a cuprous compound and its solution in the cupric salt. The formation of a cuprous salt by gentle ignition of cupric sulphate in the air is far from probable; but for fear that such a reaction had taken place, the solution of the cupric sulphate was usually exposed to the air from twelve to twenty-four hours before filtration. The fact that exposure to the air for a long time after filtration caused no further formation of precipitate is a satisfactory proof that no cuprous salt remained in solution, even if it had been formed in the first place.

The outcome of all these more or less indirect experiments points to the conclusion that cupric sulphate retains about 0·12 per cent of its water of crystallisation, even when heated to 400° C. This last trace of water is given off only at a temperature at which the cupric sulphate itself begins to decompose. It must be admitted that the evidence upon the point is not absolutely certain, but there is no doubt of its great probability. Upon such a matter as this it is difficult to see how more definite results could have been procured.

Total Percentage Composition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

	Per cent.
Water lost at 360—400°	= 36·067
“ “ between 400° and redness	= 0·042
Copper, average	= 25·449
SO_4	= 38·436
Total	= 99·994

If the amounts of copper and sulphuric acid supposed to be lost during the electrolysis are added, the total becomes 100·004.

Either of these total results is now accurate within the limits of error of ordinary analysis. But it will be seen that the total percentage of crystal water indicated by the analysis is much too large as compared with the sulphuric acid, which is our only certain standard of reference. This excess of water must have been occluded in the original crystals, which were not very finely powdered. Accordingly two specimens of the purest cupric sulphate were much more finely pulverised, and their loss of weight at 400° was then found to be 36·057 (average of Experiments 21 and 23) instead of 36·067 per cent. Mr. H. M. Richards kindly measured many diameters in the two powders, and found that the particles of the coarser powder approximated one-tenth of a millimetre, while those of the finer were less than one-hundredth. Since more than half an hour's continuous powdering, at the very slow rate adopted to prevent warmth from friction, had been necessary to reduce a small amount of material to the finer state, it was concluded to abandon the attempt at obtaining cupric sulphate free from occluded water.

It must be remembered that the salt had been very slowly crystallised by the evaporation of the solution, and of course had had every opportunity to imprison traces of the mother liquor. Crystallisation from hot solutions could not be adopted because of the risk of the formation of basic salt (Hampe, *loc. cit.*). But even if the true amount of the water of crystallisation could have been determined, it would have been of little present use for the determination of the atomic weight of copper, because of the uncertainty of its molecular weight. It is hoped that an investigation of the quantitative relations of water in other compounds may be in progress during the coming year at this laboratory.

(To be continued.)

REDUCING AGENTS OF THE AROMATIC SERIES
WHICH ARE CAPABLE OF DEVELOPING
THE LATENT PHOTOGRAPHIC IMAGE.

By A. and L. LUMIERE.

AUTHORS have endeavoured to apply to photography the conquests of chemistry and to find a chemical theory for developers; from their observations the following conclusions have been drawn.

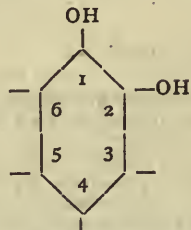
1. For a substance of the aromatic order to be a developer of the latent image there must be in the benzinic nucleus at least two groupings of hydroxyl or two of amidogen, or at the same time a hydroxylic and an amidogenic group.

2. The preceding condition is necessary, but it only seems sufficient in isomerism.

For example, orcinol will not develop; its isomeride, toluquinone, develops perfectly. Resorcinol indicated as developer has no action in the state of purity. Caffeic acid, however,—



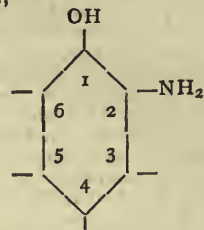
and pyrocatechin,—



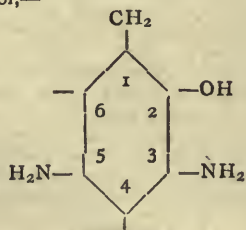
are developers. It is possible that other substances than the isomerides have reductive qualities, but these exist in all cases of isomeric relation.

3. The developing power may persist when in the molecule there are a greater number of groupings OH or NH₂.

Pyrogallol was already known; we may also mention diamidophenol,—



diamidocresylol,—



a triamidocresylol; gallamic acid.

4. When the molecule results from the welding of two or several benzinic nuclei, or of benzinic nuclei and others, the preceding remarks are only applicable when the hydroxylic groups and the amidogenic exist in the same aromatic nucleus.

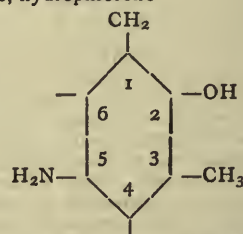
For example, benzidine has no action nor oxycarbo-styryles, whereas paradihydroquinoline acts.

5. The substitutions made in the group OH or the group NH₂ destroy the developing properties whenever at least two of these groups do not remain intact in the molecule.

For example, dimethylparamidophenol does not develop, neither does dimethylhydroquinone. Guaiacol, however acts.

6. The other substitutions which may be made in the CH of the nucleus do not seem to suppress the developing power.

For example, hydrophlorone—



Podocarpic acid does not seem to annul the developing power. But the acid function seems to diminish it, for caffeic, protocatechuic, and amidosalicylic only develop with a strong base, the alkaline carbonates being no longer sufficient.

7. The preceding remarks only apply to the aromatic series.

Ethylendiamine and guanidine have no action. Phenylhydrazine is an exception, but, on the other hand, this compound is quite outside of the previous rules by its mode of formation.

The following conditions must be added to the above. The substance must be soluble in water, its solution little coloured, and the products of its oxidation in the bath must have little colour and not dye gelatin.

In a note in the June number of the *Bull. de la Soc. Française de Photographie* the authors indicate the following formulæ for the application of paramidophenol to the development of gelatino-bromide of silver.

I.

Water	1000
Sulphite of soda	200
Carbonate of soda	100
Paramidophenol	12

II.

Water	1000
Sulphite of soda	200
Carbonate of lithia	12
Paramidophenol	12

The first formula is very energetic and is particularly suitable for instantaneous developments.

The slight solubility of paramidophenol does not give the latitude in the formulæ which pyrogallol presents, for example. But, per contra, the solution is preserved for a long time colourless and active.

Finally, in a recent communication to the French Photographic Society Messrs. Lumière publish a comparative study on hydroquinone, paramidophenol, and ikonogene. Leaving aqueous solutions of these three compounds in the air the paramidophenol oxidates first, then ikonogene; hydroquinone resists longest.

The product from oxidation of the paramidophenol, probably quinonimide, is insoluble in water; the solution is not disturbed, but deposits a black soluble precipitate,

which turns violet in ammonia or alkali and red in nitric acid.

With ikonogene the solution is coloured deep brown, turning green in ammonia and red in nitric acid.

Finally, the oxidated solution of hydroquinone is reddish, becomes yellow in ammonia, and is discoloured by nitric acid.

These same products form in developing; those of ikonogene and hydroquinone dye gelatin yellow, which remains colourless in the case of paramidophenol. At least 25 clichés can be developed with this last substance without finding any difference from first to last; whereas with the two others as soon as some clichés have been developed the others turn yellow.

These three compounds reduce soluble salts of silver, but have no action on haloid salts except in presence of an alkali or alkaline carbonate.

The addition to the developer with paramidophenol base of bromide of potassium or hyposulphite of soda produces almost similar effects as with the other developers.

By the Reeb process, to fix the weight of necessary matter to reduce 1 grm. of nitrate of silver, the authors obtained the following numbers:—

Hydroquinone	0.07
Paramidophenol	0.14
Ikonogene	0.30

It then requires twice as much paramidophenol and four times as much of ikonogene to reduce the same weight of nitrate of silver. From a practical point of view these differences are of no importance, for the reducing agent is always in great excess as regards the salt of silver. Paramidophenol, however, seems to present these advantages. It oxidates more rapidly, and in consequence is more energetic and develops more rapidly. The products of its oxidation have no injurious effect on the image or gelatin.

The best proportions are, it seems, as follows:—

Water	500
Carbonate of potash	40
Sulphite of soda	100
Paramidophenol	8

—*Moniteur Scientifique*, Jan., 1892.

METHODS FOR MILK ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

Water.

EVAPORATE 1 to 2 grms. of milk in a tared flat dish containing from 15 to 20 grms. of pure dry sand, or without sand, until apparently dry. Transfer to air bath and dry for one hour at temperature of boiling water. Cool in desiccator and weigh rapidly to avoid absorption of hygroscopic moisture.

Total Nitrogenous Matter.

Place in a Kjeldahl digestion flask a known weight (about 5 grms.) of milk and proceed exactly as described for this method by the nitrogen reporter.

Fat; Method of Adams, Modified by Wiley.

Coils made of thick filter paper, cut into strips 2.5 by 25 inches, are thoroughly extracted with ether and alcohol or the weight of the extract corrected by a constant obtained for the paper. About 5 c.c. of the well mixed milk are placed in a small beaker, covered with a watch glass, and weighed. From a weighing bottle about 5 grms. of milk are transferred to the coil by a pipette, care being taken to keep the end of the coil held in the fingers dry. The coil, dry end down, on a piece of glass is dried at the temperature of boiling water for one hour, or better dried in hydrogen at temperature of boiling water, transferred

to a syphon extraction apparatus, and extracted by at least 12 syphonings with absolute ether or petroleum spirit boiling at about 45° C. The extracted fat is dried in hydrogen and weighed.

Alternate Method of Estimating Water and Fat in Milk.

Method of Babcock.—In the bottom of a perforated test tube is placed a clump of clean cotton; the tube is then filled three-quarters full of ignited asbestos, lightly packed, and a plug of cotton inserted over it. The tube and contents are weighed and the plug of cotton carefully removed and 5 grms. of milk from a weighed pipette run into it, and the plug of cotton replaced. The tube, connected at its lower end by a rubber tube and adapter with a filter pump, is placed in a drying oven at a temperature of 100° C., and a slow current of dry air drawn through it until the water is completely expelled, which in no case requires more than two hours.

The tube containing the solids from the above operation is placed in an extraction apparatus and exhausted with ether in the usual way.

The Estimation of Sugar.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:—

Reagents.—1. *Basic plumbic acetate*, specific gravity 1.97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One c.c. of this will precipitate the albumens in 50 to 60 c.c. of milk.

2. *Acid mercuric nitrate*. Dissolve mercury in double its weight of nitric acid, specific gravity 1.42. Add to the solution an equal volume of water. One c.c. of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric iodide with acetic acid*. KI 33.2 grms., HgCl₂ 13.5, C₂H₄O₂ 20 c.c., H₂O 64 c.c.

Apparatus.—1. Pipettes marked at 59.5, 60, and 60.5 c.c. 2. Sugar flasks marked at 102.4 c.c. 3. Filters, observation tubes, and polariscope. 4. Specific gravity spindle and cylinder. 5. Thermometers.

Manipulation.—1. The room and milk should be kept at a constant temperature. It is not important that the temperature should be of any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the results for analytical purposes. The temperature selected should be the one which is most easily kept constant.

2. The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required use specific gravity flask.

3. If the specific gravity be 1.026, or nearly so, measure out 60.5 c.c. into the sugar flask. Add 1 c.c. of mercuric nitrate solution, or 30 c.c. of mercuric iodide solution, and fill to 102.4 c.c. mark. The precipitated albumen occupies a volume of about 2.44 c.c. Hence the milk solution is really 100 c.c. If the specific gravity is 1.030, use 60 c.c. of milk. If specific gravity is 1.034, use 59.5 c.c. of milk.

4. Fill up to mark in 102.4 c.c. flask, shake well, filter, and polarise.

NOTES.—In the above method of analysis the specific rotatory power of milk sugar is taken at 52.5, and the weight of it in 100 c.c. solution to read 100 degrees in the cane-sugar scale at 20.56 grms. This is for instruments requiring 16.19 grms., sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk-sugar whatever instrument is employed.

Since the quantity of milk taken is three times 20.56 grms., the polariscopic readings divided by 3 give at once the percentage of milk sugar when a 200 m.m. tube is used.

If a 400 m.m. tube is employed, divide reading by 6; if a 500 m.m. tube is used, divide by 7.5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102.4 for 60 c.c. no correction for volume of precipitated casein need be made. In no case is it necessary to heat the sample before polarising.

Alternate Method.

The sugar may also be determined either gravimetrically or volumetrically by alkaline copper solution.

Estimation of Ash.

Evaporate to dryness in a weighed platinum dish 20 c.c. of milk from a weighing bottle, to which 6 c.c. of HNO_3 has been added, and burn at low red heat until ash is free from carbon.

THE IMPERIAL INSTITUTE.

ON the 18th of the present month there took place an important gathering of friends of the Institute and representatives of the Press for the purpose of examining the progress which has been already made and considering future prospects. The visitors were conducted round the building by the Secretary, Sir Frederick A. Abel, K.C.B., F.R.S., who explained all the particulars of each department. It must be admitted that though the Institute is far from complete, yet much work, and good work, has been accomplished.

The objects of the Imperial Institute, as set forth in its Charter, are simply beyond all praise, and we can only hope that they will be faithfully and vigorously carried out. To do this, however, ample funds will be required.

The one great defect of the Institution—the non-central character of its position—is fully admitted. But it is shown that to have obtained an adequate area of ground either in the East Central or West Central districts would have encroached too far upon the funds required for building, fitting up, and organising the Institution. Hence, as the less of two evils, it shares with the Natural History Department of the British Museum a "splendid banishment" to South Kensington.

The constitution of the governing body is eminently satisfactory. Anything savouring of political partizanship has been judiciously avoided, and will, we hope, remain so in future. The only point necessary will be to carefully exclude from the governorship any persons hostile to the Colonies and to India.

The resources of the Institute, which, it must be remembered, have not been supplied by the Exchequer, amount at present to £413,000. Hence, with a due regard to the magnitude of the undertaking, the governing body did not feel at liberty to accept some of the most gorgeous and expensive plans. They adopted the designs of Mr. Colcutt, which, though by no means lacking either in convenience or even in architectural beauty, were more economical. As it is, the erection of some of the most imposing features of the building, such as the Great Hall and the principal stairway, will be postponed until the available funds permit.

The principal floor, in addition to minor features, contains the British-American, the Australasian, British-African, and Indian Conference rooms. These conference rooms form one of the most important features of the Institute. They will serve as meeting and consultation places for persons connected with, or interested in, the productions and trade of the respective groups of Colonies concerned.

The first floor comprises conference rooms for the so-called "crown colonies," commercial conference rooms, and the commercial intelligence departments.

The second-floor contains a map room, rooms for the examination of samples, and laboratories.

The ground-floor provides ample space for classified commercial samples in bulk.

We may here explain the course which a business visitor, desirous of specific information, should follow. He would first visit the Gallery, where the Index Collection and illustrations of the uses of the various products will be exhibited, and by the aid of the descriptive catalogue, or of the special hand books in course of preparation, he will easily find any particulars concerning the products of which he is in search, &c. If he wishes to know more he can then fill up a blank form with the name and reference number of the product in question, and proceed by a lift close at hand to one of the sample examination rooms on the second floor. Meantime, a box containing the bulk-sample will be brought up by lift from the store-rooms on the ground-floor. The visitors' inquiry paper will, if needful, be passed to the Commercial Intelligence Department, and returned to him with any detailed information which he may require. He will also be supplied with samples of any material which he may require for private study or experiment.

We are glad to perceive a notice that the wasteful and slovenly custom of throwing away the samples when examined will not be permitted.

Closely connected with the museum of samples is the Commercial Intelligence Department, founded on the model of the Intelligence Department of the War Office. It will systematically supply to chambers of commerce, &c., commercial information and statistics. The merchant or the manufacturer will here be able to learn where he may obtain materials or produce suitable for any given purpose, and where he may find the best demand for anything which he may have to dispose of. The sample museum and the intelligence department will be worked as much for the benefit of India and the Colonies as of the United Kingdom. These departments jointly will supply a very decided want. We have often felt pain and humiliation at perceiving that some novel product of the British Empire was brought into use in alien countries sooner than in England.

The Imperial Institute will, of course, not take any direct part in the task of education, and will not, as it was at one time feared, set on foot a new system of examination. But it will actively assist in the organisation of technical instruction at home and in the Colonies, so as to keep it on a footing, at least of equality, with that existing in alien countries. "Measures will be adopted for enabling the Enquiry Department to supply to students coming to Britain from the Colonies, Dependencies, and India the requisite information and advice to aid them in selecting their place of work and their temporary homes." Provincial industrial colleges, local commercial museums, &c., will be supplied with complete, thoroughly classified, economic collections, and with all that is new in the way of natural products, from the Colonies and India. A central department of commercial geography will form an important feature in the work of the Imperial Institute. It is to be hoped that these efforts may contribute to lighten that dense cloud of ignorance, of indifference to the Colonies and India, which is one of our weak points as a nation.

If a slight digression is permissible we should suggest a reform of our school manuals of geography. In so-called political geography the notion of "quarters of the globe" is obsolete. After the study of the United Kingdom the pupil should proceed at once and on a similar scale to a survey of India, Australia, the Dominion, British Africa, &c., and he should be taught to regard the inhabitants of all these regions as his countrymen.

We are glad to find that the study of Modern Oriental Languages is organised as a branch of the Institute. The daughters of the late Colonel Ouseley, of the Bengal Army, have endowed in his memory three scholarships in

Arabic and Persian, each one of the value of not less than £50 yearly.

An Exhibition of Indian Metal Work has now been opened at the Institute. Its nucleus will consist of a representative collection formed by H.H. the Maharaja of Jeypore.

We think that any British subject worthy of the name who carefully examines into the subject will give the Imperial Institute his most earnest support.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 2nd, 1892.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

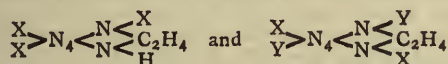
MR. WALTER N. EDWARDS was formally admitted a Member of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Duxbury, Richmond Terrace, Darwen, Lancashire; Thomas Gray, 16, Craigmore Terrace, Downhill, Glasgow; Samuel C. Hooker, Philadelphia, U.S.A.; Samuel Jackson, Nether Thong, Huddersfield; Charles Spackman, Sibley, Loughborough; Frederick William Westway, 8, Ayton Road, Stockwell, S.W.

Of the following papers those marked * were read:—

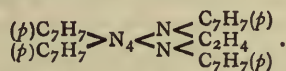
26. "Ethylene Derivatives of Diazoamido Compounds." By R. MELDOLA, F.R.S., and F. W. STREATFIELD, F.I.C.

In the same way that alkyl diazoamides can be prepared by the action of alkyl haloids on diazoamides dissolved in alcohol, together with the calculated quantity of potassium or sodium hydroxide (*Trans.*, xlix., 624; li., 102 and 434; liii., 664; lv., 412; and lvii., 784), the authors find that ethylene derivatives can be obtained by the substitution of ethylene dibromide for the alkyl haloid. The products thus obtained have the general formulæ—

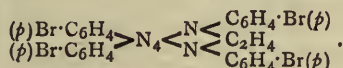


Normal ethylenediazoamide. Mixed ethylenediazoamide.

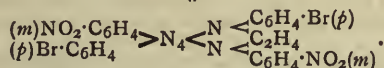
In this preliminary note it is desired only to call attention to the existence of these compounds; their detailed study will be undertaken as soon as possible. The following have been thus far prepared:—



From diazoamido-*p*-toluene. Dull orange needles; m. p., 116–117°.

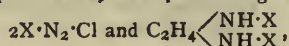


From diazoamido *p*-bromobenzene. Yellowish green needles m. p., 147°.

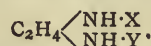


From the mixed diazoamide produced by the action of diazotised metanitriline on parabomaniline, or *vice versa*. Brownish needles, m. p. 152°.

The alkylendiazoamides are very stable, but, like the alkyl derivatives, are resolved by prolonged contact with strong chlorhydric acid at ordinary temperatures; the products of decomposition have not yet been investigated, but special interest attaches to their examination. The normal compounds may be expected to give rise to—



and the mixed compounds to $\text{X}\cdot\text{N}_2\cdot\text{Cl}$ and $\text{Y}\cdot\text{N}_2\cdot\text{Cl}$, together with a mixed substituted ethylenediamine of the type—



*27. "The Action of Light on Silver Chloride." By H. BRERETON BAKER, M.A.

The small loss in weight which silver chloride undergoes on exposure to light has led the author to investigate whether oxygen is absorbed at the same time that chlorine is evolved, Robert Hunt having long ago stated that such an absorption does take place. In the first experiments silver chloride was exposed to light in a bulb connected with a long tube standing over potassium hydrate solution; a very noticeable absorption took place. Similar experiments with oxygen, instead of air, gave similar results, showing that oxygen was the gas absorbed. Attempts were then made to find in what proportions the elements silver, chlorine, and oxygen were combined in the darkened substance, but so little of the dark substance was produced (less than 0.1 grm. in 50 grms. of unaltered chloride) that a direct analysis was found to be impossible, and an indirect method was adopted.

In the first experiments to ascertain the formula, the evolved chlorine was absorbed by potassium iodide, and the iodine which it liberated was determined; the silver was determined by treating the blackened chloride with strong ammonia, and weighing the residual metal; and the oxygen by treating the dark substance with pure chlorine and measuring the oxygen evolved. The results of one such experiment were as follows:—

	Found.	Calculated for Ag_2ClO .
Ag.. .. .	78.94	80.75
Cl	14.25	13.27
O	6.81	5.98

Other experiments were made in which the oxygen absorbed and the chlorine evolved were determined in the same apparatus. The following are some of the results:—

	Oxygen absorbed.	Chlorine evolved.
I.	1 atom.	0.70 atom.
II.	1 "	1.26 atoms.
III.	1 "	1.12 "
IV.	1 "	1.26 "

The discrepancy of the results is attributable partly to the difficulty of working with a substance which can only be obtained in small quantities, and then in admixture with a large quantity of unaltered silver chloride, and to the fact that if the analyses are not immediately performed, the determination of the formula becomes uncertain, owing to the darkened substance turning white when kept in the dark, a fresh absorption of oxygen taking place, so that probably another oxychloride is formed.

It was found that the thoroughly dried darkened substance, free from oxygen, gave an amount of water when reduced in pure hydrogen which corresponded to an amount of oxygen differing from that determined by other methods by less than 1 per cent.

If the darkened substance be really an oxychloride, it should not be produced in absence of oxygen. This was found to be the case, no darkening being observed in a vacuum or in carbon dioxide. Likewise no darkening was produced when silver chloride was exposed under pure dry carbon tetrachloride. It is to be noted, however, that carbon tetrachloride, unless carefully purified, contains substances, such as alcohol, carbon bisulphide, &c., which cause reduction of silver chloride and the deposition of black silver or silver sulphide, which darkening has hitherto been confounded with the darkening which takes place in air.

Lastly, when darkened silver chloride is boiled with pure potassium chloride, the whole dissolves, silver chloride being found in the solution together with potash

the production of alkali seems to prove that oxygen is present in the darkened substance in the combined state.

*28. "The Estimation of Slag in Wrought Iron." By A. E. BARROWS and THOMAS TURNER.

It is known that in puddling cast-iron comparatively rich in non-metallic elements, the yield of puddled bar is greater than with less impure materials, but the loss on re-heating and rolling into finished iron is also greater. It has been contended that this difference is due to intermingled slag.

The authors prepared four samples of iron, viz., best bar, best sheet from the same bar, common bar, and common sheet from the same. Pig-iron of known composition was used; the yield of common puddled bar was 6.5 per cent greater than the other, but the loss in re-heating was also 1.5 per cent greater, leaving a balance of 5 per cent in favour of the common iron. The composition of the samples was as follows:—

	Best.		Common.	
	Bar.	Sheet.	Bar.	Sheet.
Carbon	0.060	0.035	0.045	0.032
Silicon	0.228	0.168	0.275	0.221
Phosphorus ..	0.178	0.175	0.589	0.390

These results show that the silicon is equally, and very slightly, reduced in each case, while the phosphorus was much reduced in common iron, and but scarcely affected in best. This does not favour the view that much more slag is removed in one case than the other.

The authors attempted to estimate the slag by combustion in chlorine, a method already employed by one of them for cast-iron (*C. S. Trans.*, xlv., 263), but they found that the slag was attacked by the chlorine, the action taking place quite sharply at a scarcely visible red heat. A considerable number of iron ores and slags were examined, and it was found that action takes place in the sense of the equation $3\text{FeO} = \text{Fe}_2\text{O}_3 + \text{Fe}$, the iron being removed by volatilisation as ferric chloride.

This action was unexpected, and, so far as the authors are aware, has not been observed before; Deville has, however, shown that when ferrous oxide is heated in hydrogen chloride, it yields magnetic oxide of iron and ferrous chloride (*Compt. Rend.*, liii., 199).

By dissolving the iron in a cold solution of sodium copper chloride, the authors have obtained the following values:—

	Best.		Common.	
	Bar.	Sheet.	Bar.	Sheet.
Slag per cent	3.83	2.58	3.85	2.85
Loss on re-heating ..	1.25 p.c.		1.00 p.c.	

This method requires to be further examined and checked by other processes before the results can be accepted, but they are at least a fairly close approximation to the truth. Though the chlorine process is not suited for slags containing iron, it appears to be correct for cast-iron analysis, since the slag from the blast furnace seldom contains more than a trace of iron.

The authors conclude that for practical purposes the weight of slag in best and common iron may be taken as identical, and that on re-heating and rolling, each loses about the same weight of slag. The additional loss noticed on re-heating impure iron is due chiefly to the elimination of phosphorus, probably in the form of ferrous phosphate.

29. "Corydaline." II. By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER.

In confirmation of the formula proposed in their first paper (*C. S. Trans.*, 1892, 244), the authors give the results of analyses of the bromhydride and ethylsulphate ($\text{C}_{22}\text{H}_{20}\text{NO}_4 \cdot \text{C}_2\text{H}_5\text{HSO}_4 + \text{H}_2\text{O}$). The latter compound is obtained by adding sulphuric acid to an alcoholic solution of corydaline, evaporating the solution to a syrupy consistency and treating with water, when crystals of the

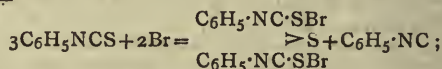
salt immediately separate out. The ethylsulphate easily dissolves in hot water, from which it crystallises, on cooling, in colourless prisms.

The alkaloid examined by the authors is identical with that obtained by Adermann (*Diss. Dorpat*, 1890; *Abstr.*, 1891, 1266) from the roots of *Corydalis cava*, by extracting with alcohol and exhausting the alcoholic solution with benzene. The two alkaloids agree in composition, in solubility, in melting-point, in their action on polarised light (dextrorotatory), and in the character of the salts which they form. On the other hand, it is quite distinct from hydroberberine, with which Adermann believed his alkaloid to be identical, or at least isomeric.

When treated with concentrated solution of hydrogen iodide, one molecular weight of corydaline gives four molecular proportions of methyl iodide and the iodhydride of a new alkaloid which has the formula $\text{C}_{18}\text{H}_{21}\text{NO}_4 \cdot \text{HI}$. The alkaloid is obtained from this salt by the addition of ammonia or potassium hydroxide, and dissolves in excess of either agent. It possesses powerful reducing properties, and dissolves in alcohol, forming a deep red-coloured solution. The conclusion that the four oxygen atoms in corydaline are united to methyl groups is confirmed by the failure to obtain any definite action with phenylhydrazine or phosphorous pentachloride.

30. "The Action of Bromine on Allylthiocarbimide." By AUGUSTUS E. DIXON, M.D.

According to Proskauer and Sell (*Ber.*, ix., 1262), bromine and phenylthiocarbimide interact, yielding an orange-red solid dibromide in accordance with the equation—



and it is further stated that the action on ethyl- and allylthiocarbimides leads to similar results. But no data of any kind are given in support of the latter statement; the author has now investigated the case of allylthiocarbimide.

Under the conditions of his experiments, viz., operating in chloroform solution, 1 mol. bromine readily unites with 1 mol. thiocarbimide, yielding dibromopropylthiocarbimide, an oily liquid, insoluble in water, soluble in alcohol, having at 17°/17° a rel. den. of 1.9712, and decomposing on distillation at ordinary pressure.

When treated with aniline it does not afford dibromopropylphenylthiourea, but the two substances interact with elimination of HBr, forming a compound of the formula $\text{C}_{10}\text{H}_{11}\text{BrN}_2\text{S}$, probably *n*-phenylbromotrimethylene-*p*-thiourea. This substance is insoluble in water, but soluble in alcohol; it melts at 103–104° (uncorr.), and is not desulphurised either on the addition of $\text{AgNO}_3 \cdot 2\text{NH}_3$ or by boiling with an alkaline solution of a lead salt.

31. "The Hydrolytic Functions of Yeast." Part I. By JAMES O'SULLIVAN.

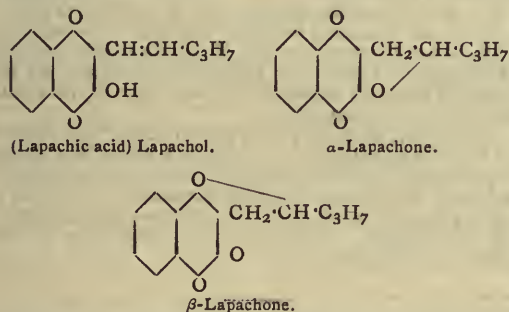
It is generally stated, on the authority of Berthelot, that the water in which yeast has been washed possesses, like yeast itself, the power of hydrolysing cane sugar, and that the active substance can be precipitated from the solution by means of alcohol. In the present communication it is shown that healthy yeast yields none of its invertase to water in which it is washed; and that when it is placed in contact with sugar, hydrolysis is effected solely under the immediate influence of the plasma of the cell, no invertase leaving the cell while hydrolysis is taking place.

After describing his mode of obtaining a healthy yeast, the author gives an account of the difficulty met with in removing the cells from the liquid in which they were suspended; although bright liquids free from organisms were obtained by adding aluminium hydrate, finings, or gypsum before filtering, such substances were found to retard the activity of the invertase, and therefore could not be used. Ultimately the object was obtained by shaking up the yeast and water with filter-paper pulp before filtering.

A detailed account is given of experiments carried out under various conditions, which show that water which had been in contact with highly active yeast for various times had no hydrolytic power, although on the addition of a mere trace of invertase the solution at once became active. The author therefore concludes that the resolution of cane sugar under the influence of yeast is entirely due to zymic hydrolysis.

*32. "The Constitution of Lapachic Acid (Lapachol) and its Derivatives." By SAMUEL C. HOOKER, Ph.D.

Lapachic "acid" is found in a crystalline state in the grain of a number of South American woods, the lapacho tree, from which it derives its name, growing plentifully in the Argentine Republic; the author has obtained his material chiefly from Surinam greenheart. Paterno, in 1882, came to the conclusion that lapachic acid (lapachol) was a homonuclear amylenehydroxynaphthaquinone, and he subsequently expressed the view that it was an α -quinone derivative, because lapachone, a neutral isomeric substance, into which it is converted by sulphuric acid, in his opinion resembled α - rather than β -naphthaquinone. The author shows that although Paterno correctly regarded lapachol as an α -quinone, his reason for doing so was wrong, as lapachone is derived from β -naphthaquinone. He proposes to term lapachone β -lapachone, to distinguish it from the isomeric pale yellow substance—a true α -quinone derivative— α -lapachone, which is obtained on treating lapachol with concentrated muriatic acid. The nature of the changes involved in the formation of α - and β -lapachones from lapachol is fully discussed in the paper, the formulæ assigned to them being as follows:—



It is shown that Paterno's isolapachone in reality contains less hydrogen than the lapachones, and that it is doubtless a β -naphthaquinonepropylfurfuran.

PHYSICAL SOCIETY.

Ordinary Meeting, June 10th, 1892.

MR. WALTER BAILY, M.A., Vice-President, in the Chair.

DR. GLADSTONE read a paper "On some Points connected with the Electromotive Force of Secondary Batteries," by himself and W. HIBBERT.

The communication includes replies to certain questions raised by M. Darrieus in a paper read before the Société Internationale des Electriciens on May 4, 1892, and to the views expressed by Prof. Armstrong and Mr. Robertson in the discussion on a paper by the present authors read before the Institute of Electrical Engineers on May 12 and 19. It also contains an account of their recent experiments on the subject.

M. Darrieus agrees with Prof. Armstrong and Mr. Robertson that the large E.M.F. immediately after charge is due to persulphuric acid, and opposes the ordinary theory that the ultimate product of discharge is lead sulphate at both plates, so far as the positive plate is concerned. The authors attribute the finding of large quantities of lead oxide by M. Darrieus to difficulties in analysis, for

it is not easy to imagine that oxide of lead could remain as such in presence of sulphuric acid. They have also shown that the changes of E.M.F. during charge and discharge coincide fairly well with those obtained by putting Pb and PbO₂ plates in different strengths of acid, and conclude "that the changes of E.M.F. depend on the strength of the acid that is against the working surface of the plates." Prof. Armstrong and Mr. Robertson disagree with the authors' views, and suppose that the sulphuric acid used was contaminated with soluble peroxides; and they also believe that H₂SO₄ itself takes part in the reactions. As regards the first objection, the authors see no reason why the traces of soluble peroxide (if any) on the plates should always vary in amount with the strength of the fresh acid in which the plates are dipped. The second point they leave an open question. In reply to the criticism on the summation of the two curves obtained respectively with two lead plates and two lead peroxide plates in acids of different strengths, they point out that the resulting curve coincides both in shape and magnitude with that determined when Pb and PbO₂ plates were placed in different strengths of acid. Whilst admitting the possibility of the lead supports having some influence on the result, they cannot conceive that such large and uniform differences as those given in their paper can be due to accidental operations of local action.

To show that the increase of E.M.F. does not depend on the presence or absence of persulphuric acid, the authors have tested the E.M.F. of a Pb and a PbO₂ plate, free from soluble oxides, in sulphuric acid of 15 per cent strength; a porous diaphragm being between the plates. The E.M.F. was 1.945 volts. After adding 1 per cent of persulphate of potassium to the liquid surrounding the PbO₂ plate, the E.M.F. was unaltered, whilst putting the Pb plate in the same liquid only reduced the E.M.F. to 1.934. Experiments had also been made on cells with phosphoric acid of different strengths instead of sulphuric acid. Changing the density from 1.05 to 1.5 raised the E.M.F. 0.176 volt, whilst calculations from Lord Kelvin's law gave 0.171 volt. In this case they consider that no acid analogous to persulphuric acid could be present. They also find that the effects of charging and repose on the E.M.F. of phosphoric acid cells are quite analogous to those obtained with sulphuric acid. The researches are being extended chiefly on the thermo-chemical side.

Prof. AYRTON thought that there was no question that the strength of acid had much to do with the changes of E.M.F. The point at issue, he considered, was whether the changes were direct effects of the strength of acid, or due to secondary actions brought about by alterations in strength.

MR. E. W. SMITH said Mr. Robertson and himself were repeating the authors' experiments with two PbO₂ plates without any grid. They had obtained results analogous to those mentioned in the paper, but the true explanation of the effects was still to seek.

MR. W. HIBBERT contended that the soluble oxides referred to by Prof. Armstrong and Mr. Robertson were not present in their experiments. They had also proved that changes in acid strength altered the E.M.F., whilst presence of persulphuric acid did not.

DR. GLADSTONE, in reply, said they also were making experiments without grids, but had not made sufficient progress to discuss them at present. Mr. Hibbert and himself believed the effects of local action inconsiderable, whilst Messrs. Armstrong and Robertson thought them very important. He hoped that ere long the points would be settled conclusively.

A paper on "Workshop, Ballistic, and other Shielded Galvanometers," by Prof. W. E. AYRTON, F.R.S., and T. MATHER, was read by Prof. AYRTON.

The galvanometers described were of the type having movable coils and fixed magnets, the advantages of which are well known. In designing the ballistic instruments, their aim had been to obtain sensibility and portability, combined with being screened from external influ-

ences, for it was often desirable to measure the magnetic fluxes and fields in dynamos by apparatus near the machines. One of the improvements adopted was the narrow coil described in a paper "On the Shape of Movable Coils, &c.," read before the Society in 1890. Such coils are particularly advantageous for ballistic instruments; for not only can greater swings be obtained by the discharge of a given quantity of electricity through such a coil than with ordinary shaped coils, when the periodic times are the same, but even when the same control is used, the same length of wire in the coil, and suspended in the same field, the narrow coil is more sensitive to discharge than coils of any other shape. Another improvement was the use of phosphor bronze strip for the suspensions instead of round wire. For a given tensile strength, both the control and the sub-permanent set could be diminished by using strip.

In February, 1888, the authors made a d'Arsonval of the ordinary type as a ballistic instrument, and found that although it was suitable for comparing condensers, for induction measurements the damping was excessive unless the resistance in the circuit was very large; this greatly reduced the sensitiveness. In 1890 they tried one of Carpentier's milliamperimeters as a ballistic instrument, but found it unsensitive. A narrow coil instrument made in the same year was found to be sensitive for currents, but as the coil was wound on copper to get damping, it was not suitable for ballistic work. In January, 1892, a somewhat similar instrument was constructed for ballistic purposes, and was found very sensitive and convenient. Although the coil had only a resistance of 13 ohms, one microcoulomb gave a swing of 170 divisions on a scale 2000 divisions distant, the periodic time being 2.7 seconds. The instrument could be used near electromagnets or dynamos, and was so sensitive that for ordinary induction measurements very large resistances can be put in series with it, thus reducing the damping to a very small amount. On the other hand, the coil could be brought to rest immediately by a short circuit key. It had the further advantage that it was not necessary to re-determine its constant every time it was used. The chief disadvantage of such instruments was the variable damping on closed circuits of different resistances. This could, however, be overcome by arranging shunts and resistances so that the external resistance between the galvanometer terminals was the same for all sensibilities.

A portable ballistic instrument, intended for workshop use, was next described. This had a narrow coil and a pointer moving over a dial whose whole circumference was divided into 200 parts. The instrument had been designed to give a complete revolution for a reversal of a flux of two million C.G.S. units, but the pointer could turn through two or more revolutions. To test stray fields, a test coil with a total area of 10,000 square centimetres is used, and has a trigger arrangement for suddenly twisting it through two right angles. The instrument then reads off directly the strength of field in C.G.S. lines. To vary the sensitiveness in known proportions resistances are employed.

Referring to the improvements made in movable coil instruments since January, 1890, when a paper on "Galvanometers" was read before the Society by Dr. Sumpner and the present authors, Prof. AYRTON said Mr. Crompton had greatly increased the sensitiveness of Carpentier's instruments by suspending the coils with phosphor bronze strip. Mr. Paul had brought out a narrow coil instrument which combined the advantages of portability, deadbeatness, quickness, and sensibility. Specimens of these instruments were exhibited. The narrow coils are enclosed in silver tubes which serve to damp the oscillations. Such a coil is suspended within a brass tube which also forms the mirror chamber, and slides down between the poles of a circular magnet fixed to the base. To damp the coil, a plug mounted on a slotted spring passes through a hole in the brass tube. A tube can be taken out and replaced by another containing

a coil of different resistance in a few seconds. An instrument of this kind, with a coil of 300 ohms, gave 95 divisions per microampère, and the damping on open circuit was such that any swing was $\frac{1}{10}$ th of the previous one.

On comparing recent instruments with those mentioned in the paper on galvanometers above referred to, a distinct improvement is apparent; for their sensitiveness is, for the same resistance and periodic time, as great as that of Thomson instruments.

Prof. PERRY remarked that the forces dealt with are extremely small.

Mr. SWINBURNE thought that ballistic galvanometers might be regarded as instruments indicating the time-integral of E.M.F. rather than quantity. Illustrating his meaning by reference to dynamos, he said that if two machines arranged as dynamo and motor were joined by wires, then if the armature of the dynamo were turned through any angle, that of the motor would move through the same angle supposing friction, &c., eliminated. Speaking of figures of merit, he pointed out that the power consumed was the important factor.

Prof. S. P. THOMPSON enquired what was the longest periods yet obtained with narrow coil instruments. The decay of magnetism in large dynamos was so slow that very long periods were required. He himself had used a weighted coil for such measurements. He also wished to know why the figures of merit were expressed in terms of scale divisions on a scale at 2000 divisions distance, instead of in angular measure or in tangents.

Mr. E. W. SMITH asked what was the length of strip required to prevent permanent sets when the deflection exceeded a revolution.

Mr. A. P. TROTTER thought that in testing magnetic fluxes by the workshop ballistic instrument, the test coil might be left in circuit instead of putting in another coil. He wished to know what error was introduced by the change of damping caused by the resistance of the circuit not being quite constant.

In his reply, Prof. AYRTON said Mr. Boys had pointed out that the scientific way to lengthen period was not by weighting the coils or needles, but to weaken the control. Periods of five seconds had been obtained. At present it was not easy to obtain longer periods, owing to difficulties in obtaining sufficiently thin strip, and to the magnetism of materials.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, June 13, 1892.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Harry Stanley Giffard; William John Heath; Mrs. Lawson; Alexander Morrison, M.D.; The Hon. William Frederick Danvers Smith, M.P.; W. Bezley Thorne, M.D.; and Captain R. H. C. Tufnell.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

The special thanks of the Members were returned for the following donations for carrying on investigations on liquid oxygen:—Mrs. Bloomfield Moore, £80; Sir David Salomons, Bart., £50; Charles Hawksley, £50.

Bacteriology.—Mr. W. Heinemann will publish in the early autumn a "Manual of Bacteriology," by Dr. A. B. Griffiths. It is essentially a work for the laboratory, and will be of use to chemists, sanitarians, brewers, medical men, agriculturalists, and others. It will be illustrated with 58 figures

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 23, June 7, 1892.

Products of the Residual Life of the Tissues, and in particular of the Muscular Tissue separated from the Living Being.—Arm. Gautier and L. Landi.—Fresh meat, even when protected from any change due to external ferments is gradually acidified. This change is due on the one hand to the formation of a small quantity of butyric and acetic acid; on the other to an incipient peptonisation of the albumenoids, and thirdly, to the formation of a little nucleine. There is formed a soluble albumenoid or myoalbumen, a substance presenting all the characters of the caseine of milk. Nearly 9 per cent of the albumenoids of fresh meat disappear and are changed into basic substances, alkaloids. The gelatinisable matters, peptones, and extractive substances do not appreciably vary in proportion.

New Methods of the Formation of Certain Substituted Imides.—A. Haller.—Phenylcarboimide, in consequence of its ready conversion into symmetric diphenyl-urea, is a dehydrating agent, and may in some cases be employed as such. The symmetrical disubstituted ureas readily form with the anhydrides dicarboxylic acids, substituted imides.

Basic Zinc Nitrates.—J. Riban.—The author has caused nitric acid, diluted with about an equal volume of water, to act upon pure zinc. There is first formed neutral zinc nitrate, but if boiled in presence of an excess of the metal there is produced a white precipitate of a basic salt, which is filtered off. The filtrate as it gradually cools becomes turbid, and yields successive deposits which are separated by filtration. The first portions deposited are generally formed of rhombic tables and needles; the subsequent deposits consist of very short needles grouped in stars. The composition of the latter portion is $6\text{ZnO}, \text{N}_2\text{O}_5, 8\text{H}_2\text{O}$. A compound may also be obtained of the composition $6\text{ZnO}, \text{N}_2\text{O}_5, 7\text{H}_2\text{O}$, having lost 1 mol. of water in the hot liquid.

On the Permolybdates.—E. Péchard.—The author has obtained and described the sodium, magnesium, and barium salt, and the permolybdates of the heavy metals. The existence of a peroxygenated acid of molybdenum is beyond doubt.

The Reproduction of Leucite.—A. Duboin.—The author has reproduced leucite by various reactions effected in presence of melted potassium fluoride, an excess of which acts as the solvent.

Contributions to the Study of Mineral Waters and their Preservation.—P. Parmentier.—The author has sought for means to obtain for analysis and research a water identical with that of the spring, and to operate upon well-defined liquids. With many chemists he contends that the analysis of a water should include all the principles present in the water at the moment when it flows clear from the spring. Others only take into consideration the clear portion contained in the bottles, the sediments being rejected. He considers that the mineral waters of Central France take their rise in an atmosphere of pure carbonic acid, and that no oxygen should come in contact with the bottles or the water during the process of bottling.

Fixation of Iodine by Starch.—Gaston Rouvier.—The compounds obtained by the author and by Mylius has the composition $(\text{C}_6\text{H}_{10}\text{O}_5)_4\text{I}$, or $(\text{C}_6\text{H}_{10}\text{O}_5)_8\text{I}_2$.

Preparation and Formation—Heat of Monosodic Resorcine and Hydroquinone.—M. de Forcrand.—A thermo-chemical paper not adapted for useful abstraction,

and not possessing sufficient interest for insertion in extenso.

Mechanical Determination of the Boiling-Points of Alcohol and of Acids.—G. Hinrichs.—This paper, which is purely mathematical, requires the accompanying diagram.

Thermic Study of the Bibasic Organic Acids. Methyl malonic and Methyl-succinic Acids. Influence of Isomerism.—G. Massol.—The author's conclusions are that the methyl-malonic or iso-succinic acid evolves more heat than its isomer succinic acid, and that it approximates to malonic acid. Methyl-succinic or ordinary pyro-tartaric acid evolves as much heat as succinic acid. These facts seem to follow from the consideration that in these acids, taken two by two, the distance of the two groups is the same.

An Oxidation-Product of Starch.—P. Petit.—On treating 4 parts of starch containing 20 per cent of water with 5 parts of the pure nitric acid of commerce, the author obtains a compound of the composition $\text{C}_5\text{H}_6\text{O}_5$. This substance, if thrown in fine powder into a concentrated solution of phenylhydrazine acetate, yields, at about 60° – 70° , a crystalline hydrazone.

Organo-metallic Compounds of the Aromatic Acetones.—E. Louise and Perrier.—The authors make known a new property of the aromatic acetones, that of combining with anhydrous metallic chlorides to form solid compounds of various colours, sometimes amorphous, but more frequently crystalline. One of the authors has obtained by the method of Friedel and Crafts, but with the intervention of these new compounds, a number of crystalline acetones. They also propose to examine if other halogenous metallic salts possess the same properties as aluminium and iron chlorides, and to ascertain which among the possible isomeric acetones yield by preference organo-metallic compounds.

The Chloro-Derivatives of the Isobutylamines.—A. Berg.—The author has obtained and described monochlorisobutylamine, dichlorisobutylamine, and chlorodisobutylamine. He has also studied the action of alcoholic soda and of potassium cyanide upon chlorodisobutylamine.

Researches on the Ptomaines in Certain Infectious Diseases.—A. B. Griffiths.—The author has obtained the ptomaine of glands, to which he ascribes the formula $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_6$, and that of pneumonia $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_3$. The former of these bases is poisonous; neither of them is found in normal urine.

MISCELLANEOUS.

The Atomic Weight of Oxygen.—Mr. R. Lehfeldt writes as follows in *Nature*:—"I notice that Lord Rayleigh gives the following summary of results on the atomic weight of oxygen:—

Dumas, 1842	..	..	15.96
Regnault, 1845	..	..	15.96
Rayleigh, 1889	..	..	15.89
" 1892	..	..	15.882

showing the remarkable fact that the atomic weight has been steadily decreasing for the last fifty years. I would suggest, as the explanation of this, that the increased population of the world, together with the great consumption of coal, have caused great wear and tear of these atoms, so that they are now mostly deficient in weight. It would seem, in fact, desirable that a Congress of chemists should be called to consider the question of providing for the renovation of the oxygen supply, and issuing trustworthy atoms of the standard weight, 16, as sealed patterns.—Firth College, Sheffield, June 3.

Physiology of the Invertebrata.—Messrs. L. Reeve and Co. have just published an important work, "The Physiology of the Invertebrata," by Dr. A. B. Griffiths, F.R.S.E., F.C.S. (demy 8vo., pp. 494, 81 figures). This work treats of the applications of chemistry and physics to the solution of biological problems.

MEETINGS FOR THE WEEK.

WEDNESDAY, 29th.—Society of Arts, 4. (Anniversary).

FRIDAY, July 1st.—Geologists' Association, 8.
Quekett Club, 8.

BAGILLT, FLINTSHIRE.

Highly Important Sale of Valuable Freehold and Leasehold Properties, situate at Bagillt, near to and adjoining the Bagillt Railway Station, on the Chester and Holyhead Railway and the River Dee.

TO MANUFACTURERS AND OTHERS.

MESSRS. CHURTON, ELPHICK, & CO. have received instructions to **SELL BY AUCTION**, at the Queen's Hotel, near the Chester Railway Station, on SATURDAY, the 2nd day of July, 1892, at Two for Half-past Two o'clock prompt, subject to conditions to be then produced, and in the following or such other lots as may be decided on by the vendor at the time of sale, the following Valuable **FREEHOLD** and **LEASEHOLD** PROPERTIES:—

LOT 1.

The Extremely Valuable Freehold PREMISES, known as "The Bagillt Marsh Works," adjoining the Bagillt Railway Station, the Bagillt Gutter, and the River Dee, together with the land belonging thereto, and the extensive Buildings, large Chimney, Flues, and fresh water supply thereon, comprising in the whole 7a. 2r. 17p. or thereabouts, and edged round with the colour pink on the sale plan. These works have a siding into the Chester and Holyhead Railway, and a frontage thereto of about 600 yards.

ONE EQUAL UNDIVIDED MOIETY of and in the Shipping Wharvea, Flushing Pool, and Land adjoining and near to and adjoining the last-described premises, containing 3a. 2r. 29p. or thereabouts, and coloured red on the sale plan; and of and in the gutters, openings, and conveniences for shipping adjoining thereto, jointly used for the purposes of the works of the vendors, Messrs. Newton, Keates, and Company, and of Messrs. Walker, Parker, and Company, the owners of the other moiety.

The above-mentioned Property will be sold subject to certain rights, which will be fully set out in the particulars of sale.

The Lessees' Interest in the entirety of a Piece of Land adjoining on the easterly side of a portion of the above secondly described Premises, containing 0a. 1r. 32p. or thereabouts, and coloured brown on the sale plan, leased to the vendors by the Board of Trade for a term of 31 years from the 29th of September, 1868, at a rent of 6s. per annum.

ONE EQUAL UNDIVIDED MOIETY of the Tenant's Interest in Two Pieces of Land, one on either side of Bagillt Gutter, containing together 1a. 0r. 20p., and coloured green on the sale plan, held by the vendors from the Dee Conservancy Board, under an annual tenancy at a rent of £25 per annum, of which Messrs. Walker, Parker, and Co., the owners of the other moiety, pay half.

The above lot affords a rare opportunity to a company desirous of acquiring premises whereon to carry on an extensive business, having regard to its situation and the facilities the property affords in securing access both to the railway and the River Dee, and for the deposit of waste. There are collieries in the immediate neighbourhood, where coal, slack, and coke can be obtained at pit prices. Vessels drawing 12 feet of water can come up the Bagillt Gutter on about an 18 feet tide.

LOT 2.

A **FREEHOLD ROAD** running from the main road leading from Flint to Holywell to the Bagillt Station, containing 0a. 0r. 24p. or thereabouts, and coloured purple on the sale plan. This road will be sold subject to the rights affecting it, and the purchaser will be entitled to a sum of £5 per annum, payable by the London and North Western Railway Company, for the right of user of a portion of it, and to a sum of 7s. 6d. a year, payable by Mr. Samuel Davies or his successors, in title for the right of user of another portion of it.

This lot will also be sold subject to the purchasers of Lots 3 and 4 having the right of user of the whole of the road with or without horses, carts, or carriages, but subject to their respectively maintaining and repairing in a proper manner one-half of the road co-extensive with the portions of their respective lots fronting such road.

LOT 3.

Two **COTTAGES** and **GARDENS**, in the occupation of Thomas Rowland and John Jones, containing 0a. 0r. 13p., adjoining the last-mentioned lot, and with the right to use such mentioned lot with or without horses, carts, or carriages, but subject to the purchaser maintaining and repairing in a proper manner one-half of the last-mentioned lot co-extensive with the frontage of this lot.

LOT 4.

Four **COTTAGES** and **GARDENS** at Pen-y-bont, and adjoining Lot 2, adjoining the main road leading from Flint to Holywell, in the

several occupations of Robert Williams, William Kendrick, John Roberts, and Elizabeth Pickstock, together with the Garden adjoining in the occupation of Elizabeth Pickstock, containing in the whole 0a. 1r. 7p.

This lot has an extensive frontage of upwards of 100 feet to the main road.

LOT 5.

A **COTTAGE GARDEN** and **PREMISES**, with valuable Building Land adjoining, having a frontage to the township road, containing in the whole by admeasurement 4a. 2r. 7p. or thereabouts, edged round with the colour vermilion on the sale plan, and now in the holding of John Hughes.

Under and included in this lot there are several seams of coal; the five-yard coal has been worked and the three-yard coal partly worked, but it is believed there are several other seams still unworked.

If Lot 5 is not sold it will then be divided and offered in 13 suitable building lots as shown on the plan and in the particulars.

Plans with detailed particulars as to each Lot are in preparation, and will shortly be published; in the meantime any further information may be obtained on application to Mr. HENRY S. WHALLEY, Land Surveyor, 90, Northgate Street, Chester; Mr. T. HUGHES, Copper Works, Greenfield, Holywell; Messrs. KELLY & KEENE, Solicitors, Mold; or the AUCTIONEERS, Chester.

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June 20, 1892. Town Clerk.

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EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1701.—JULY 1, 1892.

A CENTURY OF WORK ON THE DEVELOPMENT OF LIGHT FROM COAL-GAS.*

By VIVIAN B. LEWES, F.I.C., F.C.S.,
Royal Naval College.

THE hundred years which have elapsed since Murdoch made his greatest discovery, and illuminated his house at Redruth with coal-gas made in an iron kettle, has taught us many lessons; and by no means the least important chapter in the history of the century is the rapid growth in our methods not only of making gas but of burning it.

In spite of all that has been learnt, we are only on the outskirts of a true knowledge of the changes which give us our great gaseous illuminant; and although a century of experiment has taught our gas managers the best coal to use, and the best methods and temperatures for producing gas from it, still we are ignorant of the exact nature of the hydrocarbons present in the coal, which, under the influence of destructive distillation, yield the gas, and also of the changes which result in the complex residue we know as tar, and the gaseous mixture which forms the coal-gas itself. The questions still to be answered with regard to coal-gas will take long years of research for their elucidation, and I propose to-day to devote myself to a discussion of the methods we employ for the generation of the light from the gas, and to the facts we have learnt as to the causes of luminosity in flames, rather than to trespass upon a subject which still contains so many unknown factors.

When, in 1792, Murdoch first made coal-gas in his Cornish home, he burnt it as it escaped from the open end of a pipe, but quickly perceiving that a spreading of the flame gave a better light with a decrease in consumption, he fitted a thimble over the end of his tube, and by boring small holes in the thimble head caused the gas to burn in several small jets; but as his experiments progressed the form of his burner was modified, until in 1807 when fitting up the works of Messrs. Phillips and Lee at Manchester, he used two forms of burner,—the one a rough Argand, and the other “a small curved tube with a conical end, having three circular apertures or perforations of about a thirteenth of an inch in diameter, one at the point of the cone, and two lateral ones through which the gas issued, forming three divergent jets of flame somewhat like a *fleur de lys*.† This latter burner, which, from the shape of the jet, got the name of the cockspur burner, gave a light equal to two and a quarter mould candles of six to the pound, whilst the Argands used

developed a light equal to four candles of the same description.

The Argand burner had been in use for the consumption of oils for some years before the introduction of coal gas, and in its early form consisted simply of two concentric tubes fixed at the required distance apart, the coal gas being fed in between them. Soon, however, the idea arose of closing the open circular slot by a metal ring pierced with holes so as to give a circle of small jets, and even prior to 1816 the main principles of our present Argands were to be found in the burners then in use.

It was about 1816 also that the cockspur burner became converted into the cockscomb, and then into the batwing, this marking a distinct advance in the method of burning the gas; as by spreading the flame out into a thin sheet instead of having it in a solid mass as in the jet burner, the air was more uniformly and readily supplied to the burning gas, and the increased temperature of the flame due to the more perfect combustion increased the light-giving power of the burner to nearly that of the Argands then in use.

In 1820 Neilson, of Glasgow, whose name will be always remembered as the discoverer of the hot blast in iron-smelting, found that by allowing two flames to impinge upon each other, an increase in luminosity was obtained, and after several preliminary stages the union jet or fishtail burner was produced, in which two holes bored at the necessary angle in the same nipple cause two jets of gas to impinge upon one another so that they mutually splayed themselves out into a flat flame. The shape of the batwing flame was a very wide flame of but little height, whilst the fishtail flame was much higher and narrower, and although the service yielded by the batwing for each foot of gas consumed was no better if as good as that given by the batwing, yet its shape, which made it less affected by draughts, and enabled a globe to be used with it, ensured a greater amount of success for it than the batwing burner had secured.

The next twenty years was a period of improvement and gradual perfecting of the Argand and flat-flame burners, the influence of pressure and regulation of the flow of gas to the burner being gradually realised and allowed for, whilst other structural improvements were introduced later by Sugg, Bray, and others.

In 1854 a new and important departure was made by the Rev. W. R. Bowditch, who conceived the idea of utilising heat, which otherwise would have been lost, to raise the temperature of the air supply by enclosing an Argand burner by a double glass chimney so arranged that the air had to pass down between the glasses, and in its passage became highly heated. The burner itself was never a commercial success, as the high temperature so rapidly

* The Murdoch Lecture, Incorporated Gas Institute, June 15, 1892.

† Murdoch's Royal Society paper, 1808.

acted upon the inner glass as to render its frequent renewal necessary, but it marks an important era in the history of lighting by gas, as in it we find the germ of the regenerative lamps, which during the last thirteen years have revolutionised the methods for the production of high illuminating values from gas.

The first successful application of the principle was by F. Siemens in 1879, and the results he obtained were so far in advance of any previous result that others followed in his footsteps, and Clark, Grimston, Bower, and Thorp all contributed burners in which the same principles received slightly different application, and these in turn have given rise to the host of others which not only add to our power of illumination, but also threaten to increase business in the Law Courts.

About the same time that the regenerative burner was struggling into prominence, Mr. Lewis brought out a burner in which the coal-gas was burnt, mixed with air as in a Bunsen burner, and the flame was then urged by an artificial blast against a cone of fine platinum wire, which being heated to incandescence, gave a very high candle power per cubic foot of gas consumed, and this proved the forerunner of the Welsbach, Clamond, and other incandescent lights.

Having traced the gradual genesis of our present burners, we must now glance at the theories which have been from time to time advanced as to the causes which endow a flame containing those compounds which we know as hydrocarbons with the properties of emitting light, as until we have some conception of the causes which give rise to luminosity in a flame, it is impossible to arrive at any idea of how far further improvements may be expected to go, and in what direction to look for them.

Whilst this century was still in its teens Sir Humphry Davy undertook his great research which culminated in the invention of the Davy safety lamp, and during that great work he made some observations which led him to further researches upon the cause of luminosity in flames, which were embodied in his historical paper published in the *Transactions of the Royal Society* for 1817.

These researches led him to the conclusion that the luminosity of flames is due "to the decomposition of part of the gas towards the interior of the flame where the air is in smallest quantity, and the deposition of solid carbon which, first by its ignition and then by its combustion, increases in a high degree the intensity of the light."

Davy's explanation remained unquestioned until 1868, when Dr. Frankland showed that flames such as those of hydrogen in oxygen could be rendered luminous by compressing the oxygen, and that such a flame contained no solid particles as required by Davy's theory, also that the intense light emitted by phosphorus burning in oxygen, or arsenic in oxygen, could not be due to this cause, as the temperature of the flame was higher than the volatilising point of the products, phosphorus pentoxide and arsenious trioxide. The combustion of phosphorus in oxygen, for instance, giving a temperature of over 1300° C., whilst the oxide formed volatilises at between 800 and 900° C.

Dr. Frankland's research proved beyond doubt that a flame containing dense vapours might be luminous, but he failed in proving, as he claimed, that the luminosity of a coal-gas flame was due to dense hydrocarbon vapours heated to incandescence, and not as Davy had stated to separated carbon particles at a high temperature. This paper gave rise to a large number of other researches and communications on the subject, which largely increased our knowledge of the actions going on in flames and the various causes which affect them.

Dr. Frankland not only showed that flames might be luminous without containing solid particles, but advanced the theory that the luminosity in the flame of a burning gaseous hydrocarbon was due to dense hydrocarbon vapours, and pointed out that the soot deposited upon any cool substance held in such a flame contained

hydrogen. To this W. Stein replied, showing that the deposited soot contained less than 1 per cent of hydrogen, which was therefore probably only occluded by the carbon; and also that, if it had been present as a vapour in the flame, it ought, on being heated to the same temperature as the flame, to be once again volatile, which it undoubtedly is not. In the year 1874 Soret attempted to show that the cause of luminosity in flame really does depend upon the presence of solid particles, by focussing the sun's rays upon a luminous flame, and examining the reflected light by means of a Nicol prism; and rather later Burch pursued the same line of research, but employed the spectroscope for his examination of the reflected light, whilst quite lately Prof. Stokes by the same line of research has confirmed their results, all of which point conclusively to the presence of solid particles in those flames which owe their luminosity to the combustion of hydrocarbons. Heumann also in 1876 pointed out that hydrocarbon flames gave a distinct shadow, which is only the case when solid particles are present.

It is impossible to gainsay or refute the mass of evidence which has been adduced upon this point, and we must accept as proved beyond doubt that the luminous portion of hydrocarbon flames contains solid particles of practically pure carbon, which partly by their own combustion and partly by the combustion of the other gases present, are heated to incandescence and contribute at any rate a very large proportion of the luminosity of the flame.

In the present state of our knowledge I should be extremely sorry to say that the luminous portion of a flame does not contain some extremely heavy hydrocarbon vapours, and that these may not under the influence of intense heat add to the general effect, but I have been at present unable to detect their presence, whilst the presence of solid particles has been abundantly proved.

Several attempts have been made to trace the chemical changes going on during the combustion of the flame gases, and Hilgard, Blochmann, and Landolt did this by withdrawing portions of the gases from different parts of the flame and analysing them, but no definite conclusion was arrived at as to the actions which culminated in the liberation of the all important carbon particles. For some time past I have devoted myself to this point, and with the aid of my assistants have, I think, found the key to the actions which are going on within a luminous flame, actions far more complex than were imagined or provided for by the older theories and yet in themselves beautifully simple.

In our coal-gas we have a mixture of hydrocarbon gases and vapours diluted with hydrogen and small quantities of carbon monoxide, whilst such unwelcome impurities as carbon dioxide, nitrogen, and oxygen also exist in traces as small as the gas manager's skill can make them.

The composition of coal-gas varies considerably with the temperature at which the retorting takes place, and the gas made by one company may vary from time to time within fairly wide limits, whilst the composition of the London gas at the present time is a study of considerable interest, as it reveals occasionally signs of the methods of enrichment which are being tried at some of the principal works.

South Metropolitan Gas.

	1890.	1892.
Hydrogen	57.08	52.22
Unsaturated hydrocarbons . .	4.38	3.47
Saturated hydrocarbons . .	33.99	33.76
Carbon monoxide	2.63	6.23
" dioxide	0.79	0.60
Nitrogen	0.96	3.23
Oxygen	0.15	0.49
	100.00	100.00

In all our gas flames we can trace by the eye two principal zones and at least one subsidiary one. There is the non-luminous zone just above the burner, and above it again is the all important area of luminosity which gives the value to the flame, and between this and the air comes a thin non-luminous mantle which marks the confines of the flame.

The inner non-luminous zone of the flame has always been looked upon as the zone of non-combustion, and but little attention has been paid to it by the chemist, whilst the gas engineer has often yearned to decrease its size and so increase the zone of luminosity, but has so far found that regeneration is the only practical method of doing so, and if we are to increase the amount of light which it is possible to obtain from a gas flame, it is manifest that this portion of the flame offers us the most promising field for research.

My experiments upon flame gases show that as the coal-gas comes from the burner into the air, the hydrogen, on account of its lightness and diffusive power, finds its way to the exterior of the issuing gas and burns first, combining with the oxygen of the air to form water vapour; next in order of rapidity of burning is the methane or marsh gas, which is also the lightest gas next to hydrogen present; the hydrogen in the marsh gas burns to water, whilst the carbon burns partly to carbon dioxide and partly to carbon monoxide, according as the marsh gas molecule at the moment of combustion is in an excess or deficiency of air.

The carbon monoxide is generated in the flame, partly by incomplete combustion and partly by the action of water vapour on some of the heavy hydrocarbons, so much more rapidly than it is burnt, that it rapidly increases in quantity up to the top of the non-luminous zone.

The combustion of these two gases on the exterior of the lower portion of the escaping coal-gas creates intense heat, and bakes the remaining portions of the gas in the non-luminous zone, and causes important changes to take place in the heavier saturated and unsaturated hydrocarbons present. These consist chiefly of ethylene, benzene, propylene, butylene, and crotonylene, as representatives of the unsaturated hydrocarbons, and methane, ethane, propane, and probably butane, as the saturated.

With the exception of the methane these hydrocarbons are all of considerable density, and the denser they are the smaller is their tendency to find their way to the exterior of the flame, and only the straggling molecules from their ranks do this, so these bodies decrease far more slowly in the earlier portion of the flame than the lighter gases with which they are mixed.

These hydrocarbons, however, are gradually altered by the heat to which they are subjected, and all show a tendency to break up into acetylene at a temperature of a little over 1000° C. (2120° F.), so that by the time the top of the non-luminous zone is reached, 81 per cent of the still existing hydrocarbons have been converted into this body, and the luminosity of the flame commences immediately after.

Acetylene is a clear colourless gas, with a strong and disagreeable odour. It consists of 24 parts by weight of carbon, combined with 2 parts by weight of hydrogen. It is one of those bodies which, during their formation, take in heat instead of giving it out; and it is therefore called an "endothermic" compound. Such substances are especially liable to decomposition, as this is accompanied by a rise in temperature instead of, as is the case with most decompositions, an absorption of heat. Acetylene is decomposed at between 1100° C. and 1200° C. into carbon and hydrogen, together with traces of higher hydrocarbons; while Berthelot has shown it to be so unstable that it can be broken up into carbon and hydrogen by detonating a percussion cap in it.

(To be continued.)

A METHOD FOR THE QUANTITATIVE SEPARATION OF BARIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. BROWNING.

THE fact that strontium can be separated quantitatively from calcium by boiling the nitrates with amyl alcohol, as I have recently shown,† naturally suggested a similar separation of barium from calcium by the same general treatment. Solutions of specially purified barium and calcium nitrates were prepared and standardised either by the evaporation or filtration of definite portions after treatment with sulphuric acid. The mean of several closely agreeing results, both by evaporation and filtration, was taken as the standard. The method followed was essentially the same as described in the method for the quantitative separation of strontium from calcium referred to above. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon barium nitrate alone. Accordingly, definite amounts of the barium salt were measured into Bohemian beakers of about 100 c.m.³ capacity and weighed. The water was then evaporated over a water-bath, and the dry salts dissolved in a few drops of water and boiled with 30 c.m.³ of amyl alcohol, that amount being determined upon as convenient, until the normal boiling-point of the alcohol was reached—128° to 130° C. During the boiling the beaker was placed upon a piece of asbestos board about 15 c.m. square to keep the inflammable fumes of the alcohol from the flame. When the temperature of the alcohol reached its normal boiling-point the beaker was removed and the barium nitrate filtered off upon an asbestos felt in a perforated platinum crucible, the crucible and felt having been previously dried and weighed. The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a ground glass plate. The last traces of barium nitrate were removed from the beaker by washing with small amounts of anhydrous amyl alcohol contained in a wash bottle, previously described, to the mouth-piece of which a small chloride of calcium tube was connected. The crucible containing the barium nitrate was placed in an air-bath and heated to 150° C. The process of heating and weighing was repeated until a constant weight was obtained. Series I. shows the results of these experiments, the barium being calculated as oxide.

Series I.			
BaO taken.	BaO found.	Error.	
Grm.	Grm.	Grm.	Grm.
1. 0.1040	0.1039	0.0001—	
2. 0.1043	0.1043	0.0000	
3. 0.0524	0.0522	0.0002—	
4. 0.0519	0.0518	0.0001—	

These results show plainly enough the complete insolubility of the barium salt in the amyl alcohol; but to confirm them the filtrates of 3 and 4 were evaporated to dryness, ignited to burn off any organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness, and weighed. The weights in both cases showed the absence of any residue.

Series II.					
BaO taken.	BaO found.	Error.	CaO taken.	CaO found.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
5. 0.1410	0.1406	0.0004—	0.0112	0.0114	0.0002+
6. 0.1300	0.1301	0.0001+	0.0926	0.0926	0.0000
7. 0.1043	0.1049	0.0006+	0.0741	0.0736	0.0005—
8. 0.0781	0.0781	0.0000	0.0556	0.0554	0.0002—
9. 0.0525	0.0526	0.0001+	0.0373	0.0372	0.0001—

* From the *American Journal of Science*, vol. xliii., April, 1892.

† *Ibid.*, xliii., 50.

Series III.

BaO taken.	BaO found.	Error.	CaO taken.	CaO found.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
10. 0'1304	0'1308	0'0004+	0'0927	0'0921	0'0006—
11. 0'1043	0'1046	0'0003+	0'0371	0'0370	0'0001—
12. 0'1037	0'1036	0'0001—	0'0743	0'0744	0'0001+
13. 0'0783	0'0776	0'0007—	0'0427	0'0422	0'0005—
14. 0'0519	0'0521	0'0002+	0'0369	0'0361	0'0008—
15. 0'0519	0'0512	0'0007—	0'0570	0'0567	0'0003—
16. 0'0261	0'0259	0'0002—	0'0925	0'0925	0'0000

The next experiments were directed toward a separation of barium and calcium nitrates. Definite amounts of a solution of barium nitrate were measured from burettes into counterpoised beakers and weighed as already described; the calcium nitrate was then added in solution and the weight taken again. The water was evaporated, and the dry salts dissolved again in the least possible amount of water and boiled as before with 30 c.m.³ of amyl alcohol. The barium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried, and weighed as previously described. The calcium was determined in the filtrate in the form of the sulphate by evaporation of the alcohol, treatment with an excess of sulphuric acid, and ignition. Series II. gives the results of this treatment.

In Series III. the effect of a double treatment with the alcohol is recorded. In these experiments, after the first boiling already described, the alcohol was decanted upon an asbestos felt under the conditions previously mentioned, and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water, and this solution was treated with a drop of dilute nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water, 30 c.m.³ of alcohol were added, and the boiling repeated. The residue was filtered off upon the felt through which the first portion had been decanted and washed with amyl alcohol, care being taken to remove all particles from the beaker by careful rubbing. The crucible and residue were heated to 150° C. as before and weighed. The results after one treatment are fully as satisfactory as those after the double treatment,—a point which simplifies the method considerably. In the separation of strontium from calcium the double treatment was necessary. The form in which the salts separate suggested a possible explanation. The strontium nitrate separate in plate-like masses, while the barium is much more granular, and therefore less liable to include foreign matter.

Series IV. contains the results of certain experiments directed toward the separation of barium and strontium together from calcium. Definite portions of the three nitrate solutions were measured into counterpoised beakers, and the successive weights taken as previously described. The method of treatment was the same as that described in the double treatment of the barium and calcium salts. The correction for the solubility of the strontium salt was applied (0'001 grm. of strontium oxide to 30 c.m.³ of the alcohol used) in the manner defined in

the paper upon the separation of strontium from calcium. The results are tabulated for the nitrates in the cases in which barium and strontium were treated together, but the errors are also averaged on the oxides for the amounts of barium and strontium nitrates taken in order that they may be compared more conveniently with the results of the previously series.

In experiments 21, 25, 15 c.m.³ of the alcohol were used in each boiling instead of the 30 c.m.³ of the previous experiments, and thus the total amount of the corrections for the solubility of the strontium salt was reduced one-half. In experiments 21, 23, and 25 the calcium was determined by precipitation with sulphuric acid, the precipitate being filtered off, ignited at low redness, and weighed.

The rapidity of execution and satisfactory character of the results of this method of separating barium from calcium seem to place it among good analytical methods.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, June 11th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, three were found to be very slightly turbid; the remainder being clear, bright, and well filtered.

The character of the water supply to the metropolis during the month of May was not found to differ appreciably from that manifested during the two or three months preceding. The proportion of organic matter present in the water—noticeably low throughout—was found to be just a little higher in the March supply than in that of

Series IV.

Ba(NO ₃) ₂ and Sr(NO ₃) ₂ taken.	Ba(NO ₃) ₂ and Sr(NO ₃) ₂ found and corrected.	Error in nitrates.	Error averaged and calculated as oxide.	CaO taken.	CaO found.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
17. 0'3941	0'3945	0'0004+	0'0002+	0'0283	0'0277	0'0006—
18. 0'1436	0'1442	0'0006+	0'0003+	0'0568	0'0558	0'0010—
19. 0'3163	0'3152	0'0011—	0'0006—	0'0284	0'0274	0'0010—
20. 0'1978	0'1987	0'0009+	0'0005+	0'0285	0'0280	0'0005—
21. 0'1948	0'1932	0'0016—	0'0008—	0'0833	0'0835	0'0002+
22. 0'1971	0'1971	0'0000	0'0000	0'0830	0'0817	0'0013—
23. 0'1973	0'1960	0'0013—	0'0007—	0'0830	0'0824	0'0006—
24. 0'1959	0'1970	0'0011+	0'0005+	0'0830	0'0819	0'0011—
25. 0'1971	0'1963	0'0008+	0'0004+	0'0834	0'0831	0'0003—

February, but lower again in that of April, and still lower in that of the past month; this statement being applicable both to the Thames-derived and the Lea-derived supplies.

The following Table shows the smallness of the proportion of organic matter present in the Thames-derived supply, taken for illustration, and the successive, but not important, decrease in its proportion during the past three months. With the coming on, however, of any considerable rainfall, a corresponding unimportant increase in the proportion may be anticipated. The maximum proportion of organic carbon met with in any one of the 536 samples examined during the past three months, or 0.188 part in 100,000 parts of the water, corresponds as nearly as may be to a little over three-tenths of a grain of organic matter per gallon:—

	Ratio of brown to blue tint.	Oxygen re- quired for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
March ..	8.6 : 20	0.043	0.144	0.188
April ..	5.6 : 20	0.033	0.125	0.147
May ..	4.7 : 20	0.029	0.119	0.143

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

NOTE ON THE DETECTION OF CHLORINE AND BROMINE IN PRESENCE OF IODINE.

By D. S. MACNAIR, Ph.D., B.Sc. (Lond.).

WHEN freshly precipitated moist silver iodide is heated with potassium bichromate and concentrated sulphuric acid no iodine is set free, but the precipitate readily dissolves, forming silver iodate, which is precipitated, along with some silver bichromate, on diluting moderately and cooling the solution. Silver bromide, when treated in the same way, gives silver sulphate—the whole of the bromine being set free; while silver chloride behaves like the bromide, giving free chlorine and silver sulphate.

These reactions furnish an easy method of detecting chlorides or bromides in presence of iodides. It is only necessary to precipitate with excess of silver nitrate, filter off and wash the precipitate, and heat it with powdered potassium bichromate and a little strong sulphuric acid. If any chloride or bromide is present, even with a very large excess of iodide, its presence is easily detected by the evolution of chlorine or bromine.

I am at present making further experiments with a view to determining the delicacy of the reaction and also whether it can be conveniently employed for the quantitative separation of iodine from chlorine and bromine.

The People's Palace Technical Schools,
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METHODS OF DETERMINING POTASH.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

METHOD OF LINDO AS MODIFIED BY GLADDING.

1. *Superphosphates*.—Pulverise the fertiliser (200 or 300 grms.) in a mortar. Boil 10 grms. with 300 c.c. of water for thirty minutes; add ammonia in slight excess and then a little oxalate of ammonia, thus precipitating all phosphate and sulphate of lime, oxide of iron, and alumina, &c.; make up to 500 c.c., mix thoroughly, and filter through a dry filter; take 50 c.c., corresponding to 1 gm., evaporate nearly to dryness, add 1 c.c. of dilute H_2SO_4

(1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilisation of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water plus a few drops of HCl, 5 c.c. of a solution of pure NaCl (containing 20 grms. NaCl to the litre), and an excess of platinum solution (4 c.c.) are now added. This solution is then evaporated to dryness in a small dish, the residue taken up with a little water sufficient to dissolve it, and strong alcohol added. The precipitate is washed thoroughly with alcohol by decantation and on filter as usual. The washing should be continued even after the filtrate is colourless. Ten c.c. of the NH_4Cl solution prepared as directed are now run through the filter, or the washing may be performed in the dish. This 10 c.c. will contain the bulk of the impurities, and is thrown away. Fresh portions of 10 c.c. NH_4Cl are now run through the filter several times (five or six). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 gm. metallic platinum in every 10 c.c.

2. *Muriates of Potash*.—In the analysis of these salts an aliquot portion containing 0.500 gm. is evaporated with 10 c.c. platinum solution plus a few drops of HCl, and washed as before.

3. *Sulphate of Potash, Kainite, &c.*—In the analysis of these salts an aliquot portion containing 0.500 gm. is taken, 0.250 gm. of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c.c. platinum solution. In this case special care must be taken in the washing with alcohol to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colourless. Twenty-five c.c. of the NH_4Cl solution are employed instead of 10 c.c., and the 25 c.c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

4. *Organic Compounds*.—In case the potash is contained in organic compounds like tobacco-stems, cotton-seed hulls, &c., weigh out 10 grms., saturate with strong sulphuric acid, and ignite in a muffle to destroy organic matter; then proceed as under (1). To prepare the washing solution of NH_4Cl , place in a bottle 500 c.c. H_2O , 100 grms. of NH_4Cl ; shake till dissolved. Now pulverise 5 or 10 grms. of K_2PtCl_6 , put in a bottle, and shake at intervals for six or eight hours; let settle overnight; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

ALTERNATE METHODS.

Prepare the fertiliser as for the Lindo-Gladding method, take 10 grms., boil for ten minutes with 200 c.c. water, and after cooling, and without filtering, make up to 1000 c.c., and filter through a dry paper. If the sample have 10 to 15 per cent K_2O (kainite), take 50 c.c. of the filtrate; if from 2 to 3 per cent K_2O (ordinary potash fertilisers), take 100 c.c. of the filtrate. In each case make the volume up to 150 c.c., heat to 100° C., and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner, add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free of chlorides. Add to filtrate 1 c.c. strong ammonium hydrate and then a saturated solution of ammonium carbonate until excess of barium is precipitated. Heat. Add now, in fine powder, 0.5 gm. pure oxalic acid or 0.75 gm. ammonium oxalate. Filter, wash free of chlorides; evaporate filtrate to dryness in a platinum dish, and holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c.c. or more. To this filtrate, after adding two drops of strong

hydrochloric acid, is added, in a porcelain dish, 5 to 10 c.c. of a solution of 10 grms. of platinic chloride in 100 c.c. of water. The mixture is now evaporated on the water-bath to a thick syrup, or further, as above treated with strong alcohol, washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 c.c. ether, dried for thirty minutes at 100° C., and weighed.

It is desirable, if there is an appearance of foreign matter in the double salt, that it should be washed, according to the previous method, with 10 c.c. of the half-concentrated solution of NH_4Cl , which has been saturated by shaking with K_2PtCl_6 , as recommended by Gladding.

The use of the factor 0.3056 for converting K_2PtCl_6 to KCl and 0.19308 for converting to K_2O are continued.

ANALYSIS OF MOLYBDENITE, REALGAR, AND ORPIMENT.

By P. JANNASCH and V. WASOWICZ.

SOME time ago one of us had opened up several inorganic sulphides (pyrites, blende, antimonite, copper pyrites), by ignition in a current of oxygen for the purposes of quantitative analysis, and at the conclusion of the work several successful preliminary experiments were made on the use of hydrogen peroxide as an oxidising and absorbing agent in place of bromine-water.

In carrying out the following analyses of molybdenite, realgar, and orpiment, with the use of the former reagent, it was found practicable greatly to simplify and improve the process of ignition.

If the products of combustion are received in bromine-water, the excess of bromine and the hydrobromic acid formed during the reaction must be evaporated away before the sulphuric acid is precipitated, as they have a somewhat solvent action upon barium sulphate. By the use of hydrogen peroxide this loss of time is avoided. For the purposes of technical analysis the volumetric determination of the sulphuric acid by means of decinormal alkali or decinormal barium chloride is generally sufficient.

I.—Analysis of Molybdenite.

The material used was from Altenberg, in Saxony. A qualitative analysis showed the presence of molybdenum, iron, and a gangue stone.

The material, ground to an impalpable powder, was ignited in a current of oxygen in a platinum boat. Glass cylinders were used as receivers; they contained a 3 per cent solution of hydrogen peroxide free from sulphuric acid. As a third receiver we used instead of an Erlenmeyer flask a plain glass cylinder of the same height and width as the two other cylinders. Together we consumed for an analysis 150 c.c. of hydrogen peroxide. The combustion required about 90 minutes. Excessive temperatures must be avoided, as otherwise a part of the molybdic acid may sublime. To obviate this the flames beneath the boat were taken very small at first and were then gradually increased. The tiles of the combustion furnace must not be placed close together, as otherwise there easily occurs a volatilisation of molybdic acid. During the decomposition of the molybdenite white vapours escape into the receiver, and at the other end of the combustion-tube sulphuric acid collects in oily drops. As soon as the combustion is complete, the boat is withdrawn from the hot tube by means of a long wire hook. If it has been properly treated the powder in the boat has a whitish-grey colour without any greenish cast; reddish-black particles must not be present. The boat is weighed when cold, covered with ammonia, and heated for an hour upon the water-bath in a well covered porcelain capsule. The greatest part dissolves, leaving

behind a reddish powder. It was filtered off and washed first with ammonia and then with ammoniacal water. The filtrate was heated on the water-bath to expel ammonia, poured into a beaker and precipitated with a solution of mercurous nitrate. The mercurous nitrate precipitated subsides well; it is yellow, curdy, and very voluminous. After 24 hours the precipitate is filtered off and washed with a very weak solution of mercurous nitrate. The mercurous molybdate, carefully dried at 110°, is removed as completely as possible from the filter; the latter is cautiously returned to the funnel and washed with water containing nitric acid. This filtrate is evaporated in a weighed Rosé crucible on the water-bath, the bulk of the precipitate (which has been set aside) is added, and the whole is reduced to metallic molybdenum in a current of hydrogen according to the directions of Otto von Pfordten (*Zeit. für Anal. Chemie*, xxiii., 413). The precaution was observed to conduct the reduction first for half an hour over a common gas-flame, and then to apply the blast so as to avoid every loss of molybdic acid.

The current of hydrogen should be slow. A powerful ignition for almost two hours was needed before the weight became constant. The metallic molybdenum must have a perfectly homogeneous grey colour, free from yellowish particles.

For determining the residue insoluble in ammonia the reddish powder filtered off is slightly ignited and weighed. When heated in a platinum crucible with concentrated hydrochloric acid a portion (merely ferric oxide) was dissolved, leaving the gangue stone undissolved. In the filtrate the iron was determined by precipitation with ammonia. The gangue, after ignition and weighing in the platinum crucible, was heated with hydrofluoric and sulphuric acid, &c., when from 0.1232 grm. of substance there remained merely 0.0012 grm., so that the portion of the mineral insoluble in acid consists chiefly of quartz.

II.—Analysis of Realgar and Orpiment.

The orpiment was obtained from Tajova, in Hungary; the locality of the realgar was unknown. Only granules very carefully selected were used for analysis. Both minerals are very readily decomposed in a current of oxygen, even at a low temperature, and display the following behaviour. At a gentle heat they first take a dark reddish-brown colour, and melt then to a liquid of the same colour, when they burn very rapidly with a blue flame. Arsenious acid sublimes at the front of the combustion tube, and as far as possible it is driven into the receiver by a movable gas-flame. The formation of oily drops as in molybdenite is not observed, sulphurous acid being exclusively formed. The course of the analysis is the same in both cases.

After the completion of the process the porcelain boat is removed from the tube while still hot, and weighed. When moistened with sulphuretted hydrogen water containing hydrochloric acid, there appears a reddish colour, showing the presence of antimony. The residue from orpiment was only 0.2 to 0.3 per cent, and from realgar only 0.5 to 0.6 per cent, so that the authors could not examine it further quantitatively.

The hydrogen peroxide from the receivers, about $\frac{1}{2}$ litre, was evaporated down to about 140 c.c. in the water-bath, mixed with an excess of ammonia, and the cold solution precipitated with magnesia mixture (1 c.c. = 0.013 grm. MgCl_2), avoiding unnecessary excess. After 24 hours the ammonium-magnesium arseniate was filtered on a suction-filter and washed with ammonia (1 part water, 2 parts concentrated ammonia). The washed precipitate is dissolved in little hydrochloric acid, and the solution again precipitated with the addition of a couple of drops solution of magnesium chloride. The precipitate is dried at 100°, carefully removed from the filter, the latter extracted with hot highly dilute nitric acid; the solution is then evaporated to dryness in a weighed Rosé crucible. After adding the main portion of the magnesium precipitate the whole is dried in a slow current of oxygen, at

first at a very low temperature, which is gradually increased, ignited, and weighed.

After the evaporation of the ammonia in the filtrate, and adding 2 c.c. of dilute hydrochloric acid, the sulphuric acid is precipitated with barium chloride.—*Journ. für Praktische Chemie*, vol. xlv., p. 94.

ON THE INFLUENCE OF THE TEMPERATURE OF COLOURED SOLUTIONS UPON THEIR ABSORPTION-SPECTRA.*

By Dr. H. BREMER.

THE results of spectroscopic measurements, as G. Krüss has shown some years ago, may be affected by fluctuations of temperature which occur during an experiment. It was shown that, according to the temperature, varying values were found for the position of the Fraunhofer lines. This depends on the circumstance that the several parts of the measuring instrument expand unequally on a change of temperature, as also that the glass of which the prism consists possesses a different specific gravity at different temperatures, which affects its dispersive power. In order to measure accurately it is in the first place necessary for the instrument not to be exposed to any great fluctuations of temperature during the experiment, or that the observations are made at a temperature not differing greatly from that at which the apparatus has been standardised for wave-lengths.

As regards the measurement of the absorption-spectra of coloured solutions the results may possibly be affected in another manner, by variations of temperature during the experiment. If the rise or the fall of the temperature of the light-absorbing liquid to the extent of a few degrees affects the position and the intensity of the absorptions in the spectrum to a measurable extent, we must, both in the qualitative and quantitative examination of absorption spectra, always take the temperature of the absorbent liquid into account. If the determination of the coefficient of extinction of a liquid requires a considerable time, we must observe whether within such time the temperature of the solution present in the absorption-cell can be raised by 5°, 10°, or more, by heat radiating from the source of light. To decide this question H. Bremer undertook the following investigation at the instigation of Prof. Krüss.

It is known from a number of instances that the colour of solutions can be affected by the temperature. As far back as 1852 Schoenbein described the changes of colour of certain coloured solutions on heating. He observed that solutions of ferric hydrochlorate or nitrate which had a distinct tint at 20° became colourless at 0°, but had a much darker colour at 50°. Further, a deep blue (?) solution of potassium permanganate if cooled down to -50° became bright red, and was colourless at -100°. Very deeply coloured solutions of chromic acid and alkaline chromates appear of a pale yellow at very low temperatures.

In 1859 H. Schiff examined the solutions of forty salts and observed that with few exceptions they became darker if heated, blue substances least so.

Recently E. Wiedemann observed that the violet solution of iodine in carbon disulphide takes a brown colour if strongly refrigerated, and that brown solutions of iodine in the ethers of fatty acids became violet if heated to about 80°.

Gladstone first observed changes of colour in saline solutions spectroscopically. He examined solutions of ferric chloride, nickelous chloride and iodide, copper chloride and bromide, cobaltous chloride and sulpho-

cyanide, and referred the difference of the spectra of these salts to a change of chemical constitution occasioned by heat. He considers such a change excluded in the following salts, which also show a change of colour: gold bromide, cerium nitrate (red), potassium dichromate, ferrocyanide, and ferricyanide, molybdenum bichloride, platinum and palladium chlorides, and alkaline polysulphides. He observed further that the change of colour lasted only as long as the elevated temperature was maintained. In order to fix the results of this investigation he photographed the absorption-spectra of the above mentioned compounds both at the ordinary temperature and when heated, but unfortunately he recorded no determinations of the temperatures.

Especially interesting are the results of some experiments by Feussner, who submitted the spectra of ferric chloride, copper chloride, copper sulphate, copper-ammonium sulphate, potassium dichromate, nickel nitrate, cobaltous chloride, and platinum chloride to a rather closer examination. In all the solutions there appeared on heating an increase of the absorptive power, and this to a greater degree in chlorides than in other salts.

About the same time Melde observed that the spectrum of carmine, magenta, and aniline blue were independent of temperature, whilst in potassium chromate, picric acid, ferric chloride, and sodium dinitrophenylate a rise of temperature occasioned a qualitative displacement of the absorption from the blue towards the red end of the spectrum.

Similar observations were made a few years later by Houston, Morton, Hartley, Russell, Carnelley, B. Walter, and others.

All previous researches on the influence of temperature upon the colour and the absorbent power of salts have been confined to a description of the changes occurring in their general appearance; exact measurements scarcely exist as yet. The phenomena must be exactly measured the rather as not merely qualitative but quantitative spectrum analysis is more and more concerned with the elimination of possible sources of error.

For the measurements there was used a Krüss universal spectral apparatus with a symmetrical double slit, and only the single 60° prism was used. In this manner a strongly illuminated spectrum was obtained; the absorption bands came up very distinctly, as the dispersion was purposely selected moderate.

For the measurements there were selected solutions of such coloured compounds of which it is known that they are decidedly dissociated by heat, or the colour of which, when heated, seems even to the naked eye to undergo a decided change.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 303).

The Atomic Weight of Sulphur.

IT is seen that the ratio between the weights of sodic carbonate and sodic sulphate found in each analysis of cupric sulphate forms a valuable check upon the purity of the first substance. Conversely, if we assume the purity of each of the substances and the molecular weight of one of them, we obtain data for calculating the molecular weight of the other. Since sulphur is probably the least definitely determined of the elements involved, the figures may be used with advantage for the calculation of its atomic weight.

* Being Part II. of "Contributions to Quantitative Spectral Analysis," in the *Zeitschrift für Anorganische Chemie*, No. 5.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences* vol. xxvi.

Molecular Weight of Sodic Sulphate.
(Weights reduced to vacuum).

No. of experiment.	Source of acid.	Na ₂ CO ₃ taken. Grms.	Indicator.	Na ₂ SO ₄ found. Grms.	Molecular weight Na ₂ SO ₄ if Na ₂ CO ₃ = 106.108.
4.	Electrolysis.	1.29930	M. O.	1.74113	142.189
6.	"	3.18620	Av.	4.26790	142.131
11.	Distillation.	1.01750	M. O.	1.36330	142.169
12.	"	2.07680	M. O.	2.78260	142.169
7.	Electrolysis.	1.22427	Av.	1.63994	142.133
17.	Distillation.	1.77953	Phth.	2.38465	142.189
17.	Electrolysis.	2.04412	Phth.	2.73920	142.189
38.	Distillation.	3.06140	Phth.	4.10220	142.180

Average molecular weight of Na₂SO₄ .. 142.169

Average omitting Experiments 4, 6, and 7,

which are less reliable than the others 142.181

The first column in this table indicates the original number of the experiment. The data of Experiments 17 and 38 are given for the first time. The second column shows the source of the acid. The third column gives the weights of sodic carbonate taken; while in the fourth are recorded the indicators used in determining these weights, the abbreviations standing for methyl orange, phenolphthalein, or the average of the two. The last two columns contain respectively the weight in grms. and the molecular weight of the sodic sulphate. Since half of the results were obtained with methyl orange, it is unnecessary to correct the result for the trace of impurity in the sodic carbonate.

Subtracting from the averages the quantity Na₂O₄ = 110.106 we obtain two values for the atomic weight of sulphur:—

From the first average .. S = 32.063

" second .. S = 32.075

Usually accepted value .. S = 32.06

A large alteration in the assumed atomic weight of sodium would of course make very little difference in the result, while an alteration of 1/1000 of its value in the atomic weight of carbon changes the atomic weight of sulphur by only about the twentieth of one per cent. Although it is certain that the results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur, the outcome of the comparison is nevertheless an interesting check upon the work previously described.

The check just mentioned proved that the sodic carbonate contained the normal amount of carbon dioxide, but does not prove the absence of a very small amount of neutral impurity from the salt. Such impurity would have but a slight effect upon the ratio of the weights of the two compounds. It is true that this effect would be to diminish instead of to increase the observed atomic weight of sulphur; but it was thought advantageous to attempt the comparison of the sodic carbonate with some salt having a very different equivalent weight, in order to obtain more light upon this point. Accordingly the material to be investigated was converted with suitable precautions into sodic bromide. In Experiment 39, 1.2198 grms. (in vacuum) of sodic carbonate yielded 2.3685 grms. (in vacuum) of the bromide; or—



Upon its face the result was very satisfactory, but the great hygroscopic power of sodic bromide and various other complications afforded a wide possibility of error; hence the experiment was not repeated. To be of value, any such determination must be made the subject of an especial investigation; and for this, with so remote a purpose as the present one, time was wanting.

The Atomic Weight of Copper.

The calculation of the atomic weight of copper from the amount of metal contained in cupric sulphate which

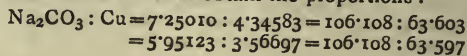
has been dried at 250–270° gives the value 63.35. This result sufficiently approaches Hampe's (63.32) to show the identity of the materials used. But it has been proved that such cupric sulphate still contains a comparatively large amount of water; and this fact renders useless the careful analyses made in 1874. The effect of the correction is considered in a following paragraph.

Besides this method of calculation "from difference," the data which have been given afford twelve other ratios for the computation of the atomic weight of copper. Six of these ratios are useless because of the known error in the crystal water; namely, 5H₂O : Cu;—SO₄.5H₂O : Cu;—5H₂O : CuSO₄;—Na₂CO₃ : CuSO₄.5H₂O;—Na₂SO₄ : CuSO₄.5H₂O;—and BaSO₄ : CuSO₄.5H₂O. Three of these last ratios give values which are much too low, and the other three give values which are much too high, as would naturally be expected. The mean is curiously near to the true value, but need not be further discussed. Neglecting these results because of the known constant error which vitiates them, there still exists seven ratios which do not involve the uncertain amount of the water of crystallisation.

I. From calculations based upon the results tabulated (see p. 303) anhydrous cupric sulphate is seen to contain certainly over 39.807 per cent of copper, and very probably as much as 39.832 per cent. The first number gives 63.53 as the atomic weight of copper, and this value must be regarded as the lowest possible limit. The second much more probable figure, which takes into account the water held by cupric sulphate at 400°, gives the proportion:—
(CuSO₄—Cu) : Cu = (100.000—39.832) : 39.832 =
= 96.06 : 63.593.

II. From Experiments 4, 6, 7, and 8 it is found that 7.2501 grms. of sodic carbonate correspond to 4.34583 grms. of copper when methyl orange is used as an indicator; and from Experiments 6, 7, and 8 it is found that 5.95165 grms. of sodic carbonate correspond to 3.56697 grms. of copper when phenolphthalein is used as an indicator. It has been shown that the impurities of the sodic carbonate probably rendered the latter quantity of the salt about 0.007 per cent too high; hence the true weight should have been 5.95123. The correction is so small that it has not heretofore been applied.

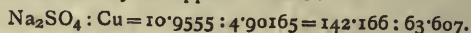
From these values we obtain the proportions:—



Average 63.600

The highest individual result was 63.604, the lowest 63.592, when entirely uncorrected.

III. From Experiments 4, 6, 7, and 9 it is apparent that 10.95552 grms. of sodic sulphate are equivalent to 4.90165 grms. of electrolytic copper. Hence:—

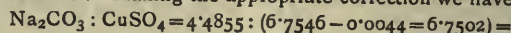


Highest value 63.614

Lowest 63.595

The last determination (Experiment 9) is by far the most trustworthy. The value deduced from it is 63.600.

IV. From Experiments 4 and 6 it is evident that 4.4855 grms. of sodic carbonate (average) are equivalent to 6.75463 grms. of cupric sulphate which has been dried at 360°. But it is reasonably certain that this cupric sulphate still contained sixty-six hundred-thousandths of its weight of water. Making the appropriate correction we have:—



= 106.108 : 159.681.

Highest value 159.703

Lowest 159.673

Subtracting SO₄ = 96.060, the average value Cu = 63.621 is obtained.

V. In the same way, from Experiments 4, 6, and 9, 9.31558 grms. of sodic sulphate are seen to correspond

with $10\cdot4715 - 0\cdot0069 = 10\cdot4646$ grms. of really anhydrous cupric sulphate. Hence:—

$\text{Na}_2\text{SO}_4 : \text{CuSO}_4 = 9\cdot3156 : 10\cdot4646 = 142\cdot166 : 159\cdot701$.
Highest value 159'73
Lowest 159'65

From the average, $\text{Cu} = 63\cdot641$. This result has a very large probable error, in the chemical as well as in the mathematical sense.

VI. and VII. Only one experiment was made with baric sulphate, but the result is appended for the sake of completeness. From No. 10 it is seen that 100'000 parts of crystallised cupric sulphate are equivalent to 93'289 parts of baric sulphate. But the same amount of the same specimen of the salt had been shown to contain 25'448 parts of copper and 36'109 parts of water. (See vol. lxxv, pp. 282 and 303). From these data:—

VI. $\text{BaSO}_4 : \text{Cu} = 93\cdot289 : 25\cdot448 = 233\cdot16 : 63\cdot603$.

VII. $\text{BaSO}_4 : \text{CuSO}_4 = 93\cdot289 : 63\cdot891 = 233\cdot16 : 159\cdot685$.

From the last value $\text{Cu} = 63\cdot625$. The atomic weight of barium probably lies between 137'0 and 137'2; the mean value is assumed above. The corresponding variations of the atomic weight of copper would be from 63'57 to 63'63 with the first ratio, and from 63'54 to 63'69 with the second.

The results of the seven ratios dependent upon the analysis of cupric sulphate are collected in the following table.

The Atomic Weight of Copper.

Ratio.	Lowest.	Highest.	Experimental mean.
I. $(\text{CuSO}_4 - \text{Cu}) : \text{Cu}$	[63'53]	[63'62]	63'593
II. $\text{Na}_2\text{CO}_3 : \text{Cu}$	63'592	63'604	63'600
III. $\text{Na}_2\text{SO}_4 : \text{Cu}$	63'59	63'61	63'607
IV. $\text{Na}_2\text{CO}_3 : \text{CuSO}_4$	63'61	63'64	63'621
V. $\text{Na}_2\text{SO}_4 : \text{CuSO}_4$	63'59	63'67	63'641
VI. $\text{BaSO}_4 : \text{Cu}$	[63'57]	[63'63]	63'603
VII. $\text{BaSO}_4 : \text{CuSO}_4$	[63'54]	[63'69]	63'625
Average			63'612
Average, omitting V. and VII. for obvious reasons			63'605

The correction of the experimental mean, in each case, for the amount of copper and sulphuric acid lost during electrolysis, diminishes the variations noticeable above to a remarkable degree. But since the validity of this correction is doubtful, and since its application scarcely influences the two most important results (II. and III.), the figures have been allowed to stand uncorrected. The final average would have remained essentially the same. The highest and lowest values given in this table are in several cases much more seriously in error than the actual experimental results. The reasons for this widening of the limits will be sufficiently understood through a careful perusal of the matter which immediately precedes the table.

Changes in the atomic weights of the elements used as standards of reference of course cause slight changes in the corresponding atomic weights of copper. Sulphur enters into a larger number of the ratios than any other element, excepting, of course, oxygen and copper; but a reasonable change in its assumed atomic weight, while slightly affecting individual results, has no effect upon either of the averages. Carbon and sodium are both determined with a high degree of accuracy, and oxygen is our standard of reference. A fuller discussion of these results will be found in the concluding summary.

(To be continued).

The Reddening of Carboic Acid.—E. Fabrini (*Pharm. Post and Chemiker Zeitung*).—According to the author the reddening depends on the action of hydrogen peroxide in presence of metals and ammonia. Pure carboic acid is not coloured by hydrogen peroxide.

NOTICES OF BOOKS.

Alkali, &c., Works' Regulation Act, 1891. Twenty-Eighth Annual Report on Alkali, &c., Works, by the Chief Inspector. Proceedings during the year 1891 presented to the Local Government Board and to the Secretary for Scotland. London: Her Majesty's Stationery Office.

This report is a highly interesting document, satisfactory as showing that the Act is being effectively and judiciously worked, but far from reassuring in the light it throws on the position and prospects of the heavy chemical trades. The total number of works in England scheduled under the Act is slightly increasing, viz., 787 in 1889, 791 in 1890, and 798 in 1891, but the alkali works, strictly speaking, are becoming fewer. In 1890 there were 117 in action, but during last year the number fell to 113. Including Scotland there is a total of 1048 works, 129 of which are alkali works.

The manufactures under inspection are alkali, hydrochloric acid (cylinder process), copper (wet process), cotton carbonising (alkali), sulphuric acid, chemical manures, gas-liquor, nitric acid, sulphate and muriate of ammonia, chlorine and bleaching-powder, sulphur recovery, salt, and cement.

The inspectors have made during the year 4793 visits (which may be made at any time of the day or night, and of which no previous notice is given), and have executed 4863 tests or practical analyses of escaping gases.

It is interesting to learn that manufacturers greatly prefer the Government inspector to the inspector of nuisances employed by the local authority. The maximum quantity of hydrochloric acid permissible in flue or chimney gases is 0'2 grain per cubic foot. Last year the amount actually escaping was only 0'081 grain.

Another requirement of the Act is that of the total hydrochloric acid liberated in any work not more than 5 per cent may escape. The proportion actually escaping is less than one-half of this limit. The total weight of salt consumed in the alkali manufacture in the United Kingdom was last year 846,391 tons. Of this gross amount 567,863 tons were consumed in the Leblanc process, and 278,528 in the ammonia-soda procedure. The latter amount seems growing from year to year.

The annual production of ammoniacal salt is steadily increasing. In 1889 it was 133,604 tons; in 1890 134,257 tons, and last year 143,606 tons. It is obtained as a by-product from gas-works, iron-works, shale-works, and coke and carbonising works. The author even informs us that "there are cases where more of the capital in an iron-smelting work is devoted to the collection and treatment of the tar and ammonia than to the production of the iron itself, and more profit is yielded by the former than by the latter. In some cases iron has become the by-product of an iron-smelting work, yielding the place of main product to the ammonia."

Much progress has been effected in the treatment of vat waste by the Chance-Claus process; 80,000 tons of sulphur have been extracted from this waste at a remunerative figure, and the present yield of 900 tons weekly is valued for its purity. The inspector has been assured that at St. Helens the United Alkali Co. will desulphurise their waste within six months, and at Widnes within twelve months.

As regards chlorine a promising attempt is being made to utilise the oxidising power of nitric acid in place of that of manganese binoxide for decomposing the hydrochloric acid.

It is here justly pointed out that the sulphurous acid which contaminates the air of Widnes and St. Helens is more largely due to the combustion of coal than to the operations of the chemical works. The sulphur converted yearly into sulphuric and sulphurous acids at St. Helens is 36,108 tons, of which only 575 tons is due to the chambers and the alkali-works, and 620 tons to the

Chance-Claus process, whilst the smelting-works and glass-works account for 19,313 tons, and the coal burnt to 15,600 tons. Hence the portion coming within the purview of the Alkali Act is little more than $\frac{1}{3}$ per cent of the whole. In good truth the chemical manufacturer has been made into a scape-goat!

A very sad accident occurred in July last at the Friar's Goose Alkali Works on the Tyne, and proved fatal to seven men, some condensing towers having become dried up and ignited, fell down, burying the workmen engaged. The case was unprecedented, but special arrangements against its recurrence have been adopted by the United Alkali Company.

There is nothing in the Report from which the depressed condition of the cement industry in Kent and South Essex could be inferred. In the latter district one quite new work has come to the hammer, and in others production has been restricted.

A Treatise on Earthy and other Minerals, and Mining.
By D. C. DAVIES, M.E., F.G.S. Third Edition, thoroughly Revised and Enlarged by his Son, E. HENRY DAVIES, M.E., F.G.S. London: Crosby Lockwood and Son.

THIS work, now in its third edition, concerns itself mainly with the non-metallic minerals. We learn from the preface that it has been enlarged by about 60 pp., whilst there have been added about thirty new illustrations. Taken as a whole it decidedly merits the favourable opinion of the technical and scientific press as well as of the public. Certain omissions may, however, be specified in view of a probable new edition. Thus, among the localities for opal, Queensland probably at present occupies the first place. No mention is made under Bauxite of an aluminium terhydrate found at Irish Hill, and admirably suited for the manufacture of aluminous salts. The important deposits of asbestos in Canada might have been usefully noticed.

The account given of the Cheshire and Worcestershire salt deposits and their working in the olden time is extremely interesting. We think, however, that the potassium minerals kainite, carnallite, &c., might have been more fully noticed. We are at present practically limited to one source for these products, and we would suggest that they should be carefully sought for in India and the Colonies.

Comparatively little is said concerning the production of borax in California.

Unless the quarrying of alum shale and the manufacture of alum at Whitby have been lately resumed, they must be pronounced non-existent. When we visited the locality in 1875 we found the quarries forsaken and the works dismantled and falling to decay. The richer deposits of alum-shales at Campsie, near Glasgow, have been abandoned, as in preparing a pure alum the proprietors find it more advantageous to use china-clay or bauxite as a raw material.

As regards the composition of coprolites we may mention finding in a sample a fragment of wood, distinctly characterised by its microscopic structure, but not less rich in phosphoric acid than the accompanying animal remains.

The author's suggestion for the utilisation of the lignite of Devonshire are of the highest importance. As yielding a smokeless fuel in the form of briquettes, it should receive attention now the smoke question is coming to the front.

As a source of sulphur the pyrites from the coal-beds known as "brasses," are available only for the manufacture of ferrous sulphate. Attempts to burn them in the kilns of the sulphuric acid works have proved disastrous. The possible production of arsenic in the world seems largely in excess of the rational demand.

The recently discovered deposit of uranium (uranite) in Cornwall seems to have escaped the author's attention.

The chief defect in this work is one for which Mr.

Davies is in no way responsible. We refer to the lack of precise information concerning the mineral resources of the Colonies. This point concerns us most closely, and it is a matter to be regretted that correct data are not supplied by local geologists, mining engineers, and prospectors.

CORRESPONDENCE.

THE INTERNATIONAL COMMISSION FOR THE REFORM OF CHEMICAL NOMENCLATURE.

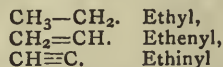
To the Editor of the Chemical News.

SIR,—The whole chemical world must feel themselves greatly indebted to Dr. Armstrong for the admirable explanation of the proposed new arrangements for naming organic compounds, and for the copious illustrations he gave on Thursday, June 16, at the meeting of the Chemical Society.

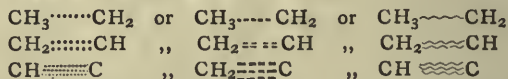
As Dr. Armstrong has ably put forward, doubtless the end and aim of nomenclature is to establish an exact and definite way of speaking and thinking; in fact, to bring chemistry itself, by means of its language, even nearer to a mathematical basis than it is now.

As Professor W. K. Clifford pointed out before the Chemical Society some years ago, the operations to be symbolised, or the methods of aggregation to be thought of and expressed by symbols, have reference to additions and multiplications, but not to the raising of powers; therefore, although the conventions in chemical formulæ are modified and even altered from those accepted and made use of in algebraic formulæ, the expression H^2O or $H^2 + O$ is inadmissible, from its manifest identity in form with $a^2 + b$. Therefore it is very promising to realise that the suffix form— H_2O —is adhered to in chemical symbols.

Since the introduction of bonds to show the combining units of the carbon atom, the signs, —, =, and ≡ have been used in chemical notation, much to the inconvenience of those who have to work with the symbols of pure mathematics as well as with chemical symbols. The identity of these symbols respectively with "minus," "equals," and "is congruent with" is manifest, and the adoption of these symbols as bonds is made more unscientific and unwelcome because equals (=) occurs also in chemical notation. Take—



as examples of these false analogies. Evidently, or ---- (a series of dots or short lines), would be better to indicate the affinities or groupings of molecules; or else a wave line, as suggesting atomic or molecular vibrations. The above would then be—



I also suggest that the use of the word "cycloid" to indicate closed chains is unscientific and is employed without reference to analogy. This word signifies "shaped from a circle, or "by means of a circle," and has been taken in mathematics to mean exclusively the curve generated by a point in the circumference of a circle rolling on a straight line. The cycloid cannot be a closed curve, and has none of the properties of the circle. I propose to use the word "cycle" as more applicable; this word has been employed in astronomy to signify the period of time in which the recurrence of the series of phenomena under discussion begins again, and therefore has relation to a closed condition; one involving all possible changes of place and apparent effects in a given

time—the “cycle” in which lunar eclipses return in very nearly the same order, for instance. If this word be deemed too pedantic, “chains” and “rings” go well together, the ring is the accepted type of closed conditions, and *rings* might have their place more fitly in chemistry than cycloids.—I am, &c.,

W. H. WALENN.

9, Carleton Road, Tufnell Park, N.,
June 22, 1892.

SEPARATION OF MANGANESE FROM COBALT AND NICKEL.

To the Editor of the Chemical News.

SIR,—In a recent number of the CHEMICAL NEWS there is an article on a “New Method for the Separation of Manganese from Cobalt and Nickel,” by Mr. Paul Jannasch. The process, however, is not exactly new, as I described practically the same method and precautions in vol. lviii., p. 125, and since its appearance I have employed it almost daily with satisfactory results.—I am, &c.,

THOMAS MOORE.

Noumea, New Caledonia, May 14, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 24, June 13, 1892.

At the meeting of the Academy Prof. von Helmholtz was by a large majority of votes elected a foreign associate of the Academy vice the late Dom Pedro d'Alcantara, ex-Emperor of Brazil. It is noteworthy that Dr. Lister, Prof. Nordenskiöld, and Prof. Sir Gabriel Stokes received only one vote each.

Anhydrous Crystalline Nickel and Cobalt Fluorides.—C. Poulenc.—The author obtains at first the amorphous fluoride by the decomposition of the double ammonium fluoride, and then causes it to crystallise in presence of vapours of anhydrous hydrofluoric acid. This method is generally applicable and gives excellent results. Nickel fluoride, NiF_2 , appears in the form of elongated prisms of a fine green. It is almost insoluble in water, and completely insoluble in alcohol and ether. It is not attacked by hydrochloric, nitric, and sulphuric acids, even if hot. Its specific gravity is 4.63. If heated in presence of air it is converted into nickel oxide. Sulphur yields black nickel sulphide. Hydrogen reduces it at a red heat,—a property which the author has utilised for the determination of nickel in the metallic state. The vapour of water decomposes it, with the production of a black oxide retaining the crystalline form of the fluoride. At higher temperatures there is formed green oxide still retaining the same form. Sulphuretted hydrogen converts it at a red heat into a yellow crystalline sulphide and hydrofluoric acid. Cobalt fluoride, CoF_2 , is a rose-coloured powder, very soluble in water. It fuses without volatilisation until it reaches a temperature of 1400°. Its form is that of small ramified prisms. It is slightly soluble in water, insoluble in alcohol and ether. Its specific gravity is 4.43. Hydrochloric, nitric, and sulphuric acid attack it slowly in the cold, but more rapidly in heat.

Action of Nitric Oxide upon the Metals and Metallic Oxides.—Paul Sabatier and J. B. Senderens.—The authors have caused nitric oxide to act at a temperature always below 500°. The gas had been prepared by the action of nitric acid upon a hot concentrated solu-

tion of ferrous sulphate; it was carefully dried and not used until it was perfectly pure. Metals not oxidisable in the air, silver, platinum, &c., are not oxidised by nitric oxide. Liquid mercury, progressively heated to ebullition, remained perfectly bright. Its vapour did not undergo any oxidation even at 450°. Aluminium (in filings) is not altered. The common metals oxidisable in the air, whether taken in a fused state, in sheets or even in filings, are oxidised only very imperfectly in nitric oxide, even if heated to a dull redness: copper, iron, cadmium, zinc are only covered with a superficial layer of oxide. Lead is oxidised more rapidly, forming yellow litharge. It is not the same with metals obtained in a divided state on reducing the oxides by hydrogen; nitric oxide acts upon them at a temperature at which it is perfectly stable, and transforms them entirely into oxides which are usually different from those yielded by oxygen or by air. Reduced nickel heated to 200° in nitric oxide burns with brisk incandescence, yielding greenish yellow protoxide. In air the incandescence is less intense, and the protoxide is always mixed with black sesquioxide. Reduced cobalt, if heated to 150° in nitric oxide, yields maroon-coloured protoxide with lively incandescence. In air we obtain the black intermediate oxide, Co_3O_4 . Iron reduced from the peroxide by a prolonged heating to redness in a current of hydrogen is oxidised in nitric oxide, beginning at 200°. The incandescence is lively, and we have a blackish-grey ferrous oxide. Reduced copper is oxidised in nitric oxide at 200°, and is entirely converted into cuprous oxide, Cu_2O , of a very homogeneous cochineal red. At dull redness incandescence sets in, doubtless primed by a little oxygen which has become free; still the product is identical, but of a more brilliant colour. In air the result is a formation of black CuO . Palladium sponge previously saturated with hydrogen has no appreciable action upon nitric oxide in the cold, but at 200° there is decided incandescence. The nitric oxide is then transformed totally into water and ammonia without any simultaneous oxidation of the metal. The authors have submitted to the action of nitric oxide a number of lower oxides obtained by reducing a higher oxide by means of hydrogen.

Thermo-Chemical Study of Guanidine, of its Salts, and of Nitroguanidine.—C. Matignon.—This memoir does not admit of useful abstraction.

Researches on the Disodium Derivatives of the Three Isomeric Diphenols.—M. de Forcrand.—Also not susceptible of abridgment.

Normal Pyrotartaric or Glutaric Acid.—G. Massol.—The formation-heats of the normal organic diacids are lower than those of their abnormal isomers.

Study on the Decomposition of the Diazo-Compounds.—J. Hauser and P. Th. Müller.—The authors study the influence of the benzenic nucleus on the speed of decomposition.

MISCELLANEOUS.

Appointment.—Dr. A. P. Luff, Lecturer on Medical Jurisprudence and Physician to St. Mary's Hospital, has been appointed Official Analyst to the Home Office in the place of the late Dr. Meymott Tidy.

Deaths from Inhaling Carbonic Acid.—The new chalybeate spring at St. Mary's has demanded in a peculiar manner its sacrifices in consequence of its exceptionally high proportion of carbonic acid. In spite of prohibition three Italians engaged in the buildings penetrated into the closed spring house in order to obtain water for their dinner. The escape of carbonic acid from the well-shaft was so violent that they were stupefied, and notwithstanding immediate assistance two of them died. —*Chemiker Zeitung*.

Certain Laboratory Appliances.—W. Ostwald.—The author describes here small gas furnaces, universal supports, filter-stands and rings, drying furnaces and funnel-holders, sulphuretted hydrogen apparatus, and an excentric latch for the sliding windows of digesting-niches. All these appliances require the accompanying figures.—*Zeitschr. Anal. Chemie*, xxxi., Part 2.

The Naturalists' Society of Switzerland.—The 75th annual gathering of this Association will be held at Bâle on September 5th, 6th, and 7th, and coincides with the 75th year's jubilee of the Bâle Naturalists' Society, and with the meetings of the Swiss Geological Society and of the Swiss Botanical Society. The excursion of the former will be to the Jura, and that of the latter to the Vosges and the Black Forest. The official concluding meeting will be held at the saline springs of Schweizerhall. Applications up to August 20 are to be made to Prof. Fritz Burckhardt, 15, Munsterplatz, Bâle.—*Chemiker Zeitung*.

A Charge against Chemical Works.—Our attention has been called to the following paragraph in the *Medical Press* for the 15th inst.:—"Two men employed in cleaning out a sewer which passed through several chemical works at Widnes succumbed last week to the fumes emanating from the refuse that had accumulated. They had not yet gone into the sewer, but inhaled the gases at the mouth of the open culvert, and before they could move away they were overpowered. It is stated in the local papers that birds have been seen to fall asphyxiated when passing near the culvert." It is not stated what were the dangerous gases. It is of course possible that the drainage from some heap of tank-waste may have found its way into the sewer, and had there encountered some acid solution, giving rise to a liberation of sulphuretted hydrogen.

Determination of the Solubility of Salts.—R. Rüdorff (*Zeit. für Angew. Chemie*).—The arrangement consists of a glass 4 c.m. in height and 2 c.m. wide at the bottom, closed with a cork having two perforations. Through the one passes a narrow glass tube open at both ends, and through the other a short glass tube expanded above the cork, over which is drawn a piece of lawn held fast by a piece of caoutchouc tubing drawn over it. The upper part of this caoutchouc tube is closed by a piece of glass rod. In order to effect a determination a solution of the salt is prepared, saturated at a higher temperature, and the beaker containing the solution is then set in a water-bath of the required temperature. The observer waits until the temperature of the solution agrees with that of the water-bath, the liquid is then stirred up with the apparatus, of which only the glass rod and the narrow glass tube project above its level, and the glass rod is then for a moment drawn out of the flexible tube. A few drops of the solution flow down into the glass. The flexible tube is closed again, the apparatus is lifted up out of the bath, and cleansed by rinsing and wiping. The cork is removed, the glass is closed with a ground stopper, and the solution which has entered is weighed. On determining the quantity of the dissolved body present its solubility is found.

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The NEXT ANNUAL GENERAL MEETING will be held at EDINBURGH, commencing on Wednesday, August 3.

President Elect—

SIR ARCHIBALD GEIKIE, LL.D., D.Sc., For. Sec. R.S., F.R.S.E., F.G.S., Director-General of the Geological Survey of the United Kingdom, Corresponding Member of the Institute of France.

NOTICE TO CONTRIBUTORS OF MEMOIRS.—Authors are reminded that the acceptance of memoirs and the days on which they are to be read are, as far as possible, determined by Organising Committees for the several Sections before the beginning of the Meeting. Memoirs should be sent to the office of the Association. Information about local arrangements may be obtained from the Local Secretaries, Edinburgh.

G. GRIFFITH,
Assistant General Secretary.

CITY AND GUILDS OF LONDON INSTITUTE.

President—H.R.H. THE PRINCE OF WALES, K.G.

Chairman of Council—The Rt. Hon. the EARL OF SELBORNE, F.R.S.

SESSION 1892-93.

The Matriculation or Entrance Examination for the CENTRAL INSTITUTION will be held on September 19-22nd, and for the Day Department of the TECHNICAL COLLEGE, Finsbury, on September 27th.

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The NEW SESSION commences on September 28th.

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The NEXT SESSION commences on October 4th. For further particulars of Day and Evening Classes, Scholarships, &c., apply at the Technical College, Leonard Street, City Road, E.C., or at the Office of the City and Guilds Institute.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1702.

THE CONDITION OF THE REACTION BETWEEN CONCENTRATED NITRIC ACID AND METALLIC NITRITES.

By V. H. VELEY, M.A.

IN the course of an experiment made with a view of saturating some concentrated nitric acid as rapidly as possible with nitrogen peroxide, a small stick of fairly dry fused sodium nitrite was placed in about 50 c.c. of the acid (sp. gr. = 1.436, percentage of nitric acid = 70 in round numbers), but after a momentary hissing no further reaction ensued, no nitrous fumes were evolved, and the sodium nitrite remained undissolved. The acid, with the nitrite, was then poured into about the same bulk of distilled water; a violent reaction took place, the effervescence of the nitrous fumes being sufficient to cause the acid to froth over the beaker, which was about half full of liquid.

The experiment was repeated several times and invariably with the same result, thus showing in a qualitative manner that for the reaction between nitric acid and sodium nitrite the presence of a certain proportion of water is necessary. It seems that the experiment above described would form a suitable and easily performed lecture illustration of the presence of water as a condition of chemical change, as also of such a change not taking place except in the presence of an electrolyte (in this case dilute nitric acid); it was thus thought of sufficient interest for the readers of the CHEMICAL NEWS.

Precisely similar results were obtained with dried potassium nitrite and re-crystallised silver nitrite, though the latter case was not so striking.

Another example is added to those already numerous of the well-known aphorism—"Corpora non agunt nisi soluta."

The University Museum, Oxford.

THE BACTERIOLOGICAL EXAMINATION OF WATER.

By DR. MAX DAHMEN.

It is probably universally recognised that the ordinary method for the bacteriological examination of water has merely a very relative value, and it is therefore not surprising if this investigation is not demanded in all cases. The known method has been elaborated by representatives of medical science, but at present the chemist is in most cases entrusted also with the bacteriological investigation of water. Here may be found a reason why relatively little weight is laid, from a medical point of view, upon the improvement of the method.

The various objections urged against the method are only too well founded. In the first place, the result, the statement of the number of the bacteria found in one c.c. of water, must be inaccurate; because, as Reinsch has shown, it is to a great degree dependent on the proportion of sodium carbonate with which the nutrient medium is neutralised, and, according to the present prescription, only a slight alkalinity is required. But the result depends, not alone on the proportion of soda, but as much on the time allowed to elapse before the enumeration of the colonies and on the species of the micro-organisms. What has been hitherto established is the scarcely approximately accurate number of the bacteria contained in

each c.c. of water, for the most part non-pathogenous. The aquatic bacteria are exactly distinguished by the fact that they are not able to vegetate at the incubation temperature; and consequently have not the property of pathogenic action. These aquatic bacteria are strictly aerobic, and are therefore developed at first only on the surface of the gelatin; the colonies which lie deeper are developed only on the third, fourth, and fifth day, as oxygen penetrates into the nutrient medium. The increase of the anaerobic species is excluded on account of the presence of oxygen, and also because, e.g., the bacillus of malignant oedema begins to vegetate only at 16°, a temperature which does not always prevail in work-rooms. The assertion of Penzo that the bacillus of malignant oedema can vegetate well even with access of oxygen in presence of certain bacteria which are *per se* indifferent, such as *Bac. prodigiosus* and *Proteus vulgaris*, does not come here into consideration, since the bacteria suspended in nutrient gelatin as isolated colonies represent pure cultures. Many other pathogenic bacteria are well known to be incapable of development at the temperature of a dwelling room.

In a bacteriological examination of the water of the Elbe, Reinsch found the optimum condition of growth at about 0.1 to 0.2 per cent of soda in the nutrient medium. For these experiments different quantities of soda were dissolved in lots of nutrient gelatin of 10 c.c. each. For a more accurate result, and to decide whether the optimum condition for growth of bacteria was the same in the water of other rivers, the author experimented on various specimens of Rhine water taken at Oberdingen. The nutrient gelatins were exactly neutralised at a boiling heat by means of soda and neutral tincture of litmus. The optimum degree of alkalinity was found to be 0.1428 per cent of soda. In further experiments, a number of test tubes, each containing 10 c.c. of neutral gelatin, received each two drops of a 10 per cent solution of soda and, in addition, one, two, three drops, &c., of a 2 per cent solution of soda. For the further experiments, the Rhine water was diluted with sterilised water. Here a proportion of 0.15 per cent was found particularly favourable for the bacteria.

In the course of the investigations it appeared that in presence of a great number of the spores of hyphomycetes the numbers of the colonies fluctuated considerably, a circumstance referable to the fact that the hyphomycetes prefer a faintly acid nutrient medium to one which is alkaline. A table has been drawn up showing that the optimum condition of growth of the micro-organisms is displaced by many colonies of hyphomycetes. If the number of colonies of hyphomycetes is subtracted from the entire number of micro-organisms, the optimum condition of growth is given at 0.15 per cent of soda.

It must here be remarked that this 0.15 per cent of soda must not be boiled with the ordinary nutrient gelatin or submitted to prolonged heat, as the nutrient medium otherwise loses the property of gelatinising.

If it has thus been ascertained in what manner the greatest number of bacteria may be found (at least, in the water above named), the question recurs: What is the purpose of knowing the number of the aquatic bacteria, since, as mentioned above, they cannot come to development at the temperature of the body, and cannot in any case become exciters of disease.

If we make use of the double capsules proposed by the author as calculated for the incubation microbe, all those micro-organisms will be excluded from development which cannot vegetate at the temperature of incubation. The colonies of most pathogenic species appear after the lapse of twenty-four hours, and may be further examined at once. These double capsules may be considered as a modification of those of Petri, from which they are distinguished by the circumstance that their hermetic closure prevents at once the evaporation of the moisture of the nutrient agar-agar necessary to vegetation, and protects against contamination by aerial germs.

The water bacteria are twenty and thirty times more numerous than those which vegetate at incubation temperature. We may obtain an approximation to the number of aquatic bacteria by subtracting the number of the colonies of those microbia which grow only at an incubation temperature from the number found by the ordinary plate process. In order to determine more accurately the number of the harmless aquatic bacteria, all the organisms which grow at incubation temperature must be diagnosed, and according as they prosper at the temperature of a dwelling room and are pathogenic, they must be deducted from the total number.

Fränkel writes: "That a drinking water, fit for use, must, above all things, be free from infectious matter has been for many years decidedly demanded by hygiene. It is not merely requisite that waters must be rejected containing bacteria which, though not pathogenic, are saprophytic. I may mention *Bacterium commune coli* (Escherich) and the *Bacillus Emmerich*. If such microbia which are by necessity inmates of the human bowels are present, the uselessness of the water will generally be also shown by chemical analysis.

Suspicious water should always be examined for pathogenic microbia or faecal bacteria, in any case for typhus bacilli. For when an epidemic of typhus has already broken out, the examination of the suspected well merely serves to confirm known facts. A water containing pyogenic microbes is unfit alike for drinking and washing, since if applied to any injured part of the body it may produce suppuration, erysipelas, or even general pyæmia. From the above it appears that a slightly alkaline water does not suffice for bringing out all the bacteria present in a water. A nutrient medium containing 0.15 per cent of soda allows the greatest number of bacteria present in rivers to arrive at development. A suspicious water, even though admissible according to chemical analysis, should be examined for pathogenic and septic organisms, especially for the bacilli of typhus, and rejected if such are present.—*Chemiker Zeitung*.

A CENTURY OF WORK ON THE DEVELOPMENT OF LIGHT FROM COAL-GAS.*

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(Concluded from p. 3).

THE next step in elucidating the cause of luminosity was to determine the temperature existing in the various parts of a flame, and as a flat flame offers a more convenient surface for research than any other, the flame from a No. 7 Bray burner was chosen, and the temperature of the various portions determined by a Le Chatelier thermo-couple.

This consists of a piece of platinum wire, the end of which is twisted with the end of a wire made of platinum with 10 per cent of rhodium. On heating this a galvanic current is generated, and this is made to pass through a reflecting galvanometer of special construction and deflects the needle; a ray of light falls upon a mirror attached to the needle, and is reflected on to a scale so that as the needle moves the spot of light travels along the scale. The scale is graduated into degrees by plunging the thermo-couple into various media the temperature of which is known, and as the current generated is practically proportional to the temperature, it makes a very convenient arrangement for measuring high temperatures.

Using this instrument, it was found that the temperature half an inch above the burner was 500° C. (932° F.), and steadily increased to 1200° C. (2192° F.) at the top of the non-luminous zone, luminosity commencing at

1200° C. (2192° F.). The highest temperature was found to be near the top of the luminous zone, where it reached 1868° C. (2462° F.). In no case is the temperature of the luminous portion of the flame less than from 1100° C. to 1200° C.

Taking the evidence which I have now laid before you, we may, I think, fairly fully explain the actions taking place in the flame and leading to luminosity.

As the gas leaves the jet the hydrogen rapidly diffuses to the outer edge of the flame and burns, the methane doing the same but rather more slowly. The combustion of these gases raise the temperature 500° C. in the first half inch, whilst before another half inch has been traversed 1000° C. is reached, and the chemical changes in the hydrocarbons are progressing rapidly, the unsaturated hydrocarbons and higher members of the saturated hydrocarbons being rapidly converted into acetylene.

If the temperature of the flame was not allowed to rise above 1000° C., this acetylene would be nearly all polymerised into benzene, diphenyl, naphthalene, and other more complex bodies, which would slowly be burnt up without liberation of carbon, and a non-luminous flame would result, as may be shown by holding a platinum dish against a luminous flat flame where luminosity disappears, but may be reproduced by heating the interior of the dish. In the case of a gas-flame, however, instead of remaining at 1000° C., the temperature rapidly rises to 1200° C., and the result is that instead of all polymerising into more complex bodies, most of the acetylene formed at once splits up into carbon and hydrogen, and the former heated to incandescence by combustion gives the luminosity, and it is the attainment of this temperature which marks the limit of the non-luminous zone.

If this were the only action, however, the luminous zone would be very short, but the bodies formed from the acetylene before 1200° C. was reached, and the methane of which some still remains unburnt, are converted into acetylene at a still higher temperature, i.e., 1300° C., and this being reached near the top of the luminous zone, yields a fresh supply of carbon and increases the height of the light-yielding portion of the flame.

In producing a luminous flame, therefore, there are two main factors to be observed, first to use such compounds as shall be most easily converted into acetylene, and secondly, to attain as high a temperature as quickly as possible. The moment we have reached this point in our theory, we naturally think how this can be best done, and find to our disgust that theory has only just caught up practice, as long experience has taught our gas managers that the olefins and unsaturated hydrocarbons are the most valuable illuminants in the gas, whilst our burner makers have slowly and by laborious steps found that by regeneration they can obtain the best results per cubic foot of gas consumed.

Some of my hearers this morning will go beyond this point, however, and it may flash through their mind to ask if acetylene is the key to luminosity, and if this gas is formed by the action of high temperatures on the gas, why is it that retorting at high temperatures gives but a trace of acetylene, and ruins the illuminating power of the gas? Simply because the heat which forms the acetylene also polymerises that body into benzene, and still more largely into naphthalene, especially in presence of carbon; and you know better than I do that high temperatures result in an increased yield of this body, and any attempts to increase the luminosity by superheating the gas must end in failure, as the action taking place in the flame is probably the only method by which this body can be so formed as to yield the desired results. In the flame it is formed and at once decomposed by the heat of the combustion; in the retort it is formed at high heats and yields but traces of benzene and naphthalene, which largely go into the tar or condense where they are least wanted.

Even if it were possible to charge gas with acetylene, it would be useless for practical purposes, as it is soluble

* The Murdoch Lecture; Incorporated Gas Institute, June 15, 1892.

in water and all other media, such as glycerin, which could be used in gasometers and meters; so that once more we come back to the fact that in our gas flame nature has provided the best methods for the carrying on of the actions which culminate in luminosity, and that the most likely field for improvement is in our mechanical treatment of the flame.

This is also shown by the fact that in an ordinary gas flame the luminosity is caused by something like 1½ per cent of acetylene liberated at the right spot, whereas double that quantity mixed with a non-luminous gas like hydrogen yields hardly any light-giving power to the flame; because by the time the temperature necessary for the splitting up of the acetylene is reached, it is nearly all burnt up without any liberation of carbon.

Regeneration, as has been before pointed out, increases to a very great extent the light yielded per cubic foot, and this is due to two causes,—in the first place by increasing the temperature, the decompositions necessary to form acetylene and liberate carbon from it are hastened, and so the non-luminous zone is decreased in size and a larger proportion of the gaseous hydrocarbons are converted into acetylene; and secondly by heating the inert nitrogen of the air supply, it prevents the withdrawal of so much heat and raises the carbon particles, when liberated, to a brighter incandescence, and so yields a higher service. Through the kindness of Mr. Siemens I have been enabled to determine the effect of regeneration on a flat flame, both as regards the diminution in size of the inner zone and the increase in luminosity.

The flame when cold had a total area of eleven square inches, of which the luminous zone occupied 7·8 square inches and the non-luminous 3·2; on regenerating this flame the total area decreased to 10·2 square inches, but the luminous zone occupied 7·9 of the space and the non-luminous only 2·3, whilst the illuminating power was increased 100 per cent.

The regenerative burner, however, is by no means the most widely used, and initial cost and domestic inertia are such all-powerful factors, that the flat flame burner is still the burner of the people; and great as have been the improvements effected in this class by our leading makers, the use of the flat flame burner means several millions wasted annually,—not to the profit of the gas manager, but simply in loss of light to the consumer, and as anything which could be done to increase the light-giving power of the flat flame would be an inestimable boon, you will pardon my spending a few moments in pointing out a direction in which I think attempts might be made to do this.

In the passage of the heavy hydrocarbons up the non-luminous zone of the flame a certain percentage must of necessity be lost by wandering into the part of the flame where combustion is taking place, and where they get burnt up without decomposition and so are lost as far as any luminosity is concerned. The larger the inner zone the greater will this loss be, so that if the inner zone can be by any means reduced in size, not only do we gain an increase on luminous surface, but a larger supply of carbon particles to yield light.

Some five and twenty years ago a device for increasing the luminosity of a flat flame called "Scholl's platinum light perfecter" created a considerable amount of interest, and undoubtedly, whilst the perfecter was new, caused a considerable increase in the amount of light emitted by the flame. The perfecter consisted of a thin slip of platinum fixed across the burner and between the orifices of the jet, so that the two streams of gas impinged upon it and afterwards mingled in the flame. The explanation always given of its action was, that in the far from perfect burners then in use, it perfected the combustion of the flame by breaking the rush of the gas, and that had it been applied to a properly regulated burner no gain would have resulted. This view is to a great extent supported by the effects of pressure upon the gain in light obtained by its use, as Mr. Rowden and Capt. Webber found that

the increase in light given by it varied from 30 per cent with a pressure of 0·46 of an inch to over 200 per cent with a small burner and a pressure of 0·84; but although this was an important factor a still more important one remained, and that this was so is shown by the fact that after using for a considerable time the perfecter lost its power to a very great extent, which would not have been the case had its action been purely mechanical.

Platinum is a metal which possesses the property of condensing gases upon its surface and rendering them chemically more active than when in their normal condition; so that if the condensed gases have a tendency to enter into chemical combination, the presence of the metal, especially when heated to a certain extent, will set up chemical action. That this is the case is clearly shown by heating a piece of platinum foil to redness, allowing it to cool until it ceases to be visibly hot, and then holding it in a current of mixed coal-gas and air, when the metal at once becomes red-hot and often reaches a temperature at which the gas is ignited. This is due to its compressing the oxygen of the air and the hydrogen of the coal-gas upon its surface and bringing about their combination,—an action which evolves great heat and raises the platinum to incandescence, although the actual temperature necessary to ignite the gas may not be reached, as the heat required to do this is very great.

In the perfecter the strip of metal, besides regulating the force with which the two streams of gas impinged upon each other, was raised by this action to incandescence in a portion of the flame which otherwise would have been several hundred degrees cooler, and thus converted the hydrocarbons into acetylene, and by its super-heating action reduced the size of the non-luminous zone. After a time, however, the platinum became attacked by the hydrocarbons of the gas, and the carbide of platinum formed ceased to have this regenerating action, and the perfecter lost its potency.

It was this deteriorating action of the coal-gas on platinum which I believe seriously militated against the success of the Lewis incandescent lamp, which was undoubtedly the most promising of its class, but which soon lost its power for this reason.

By placing a platinum wire in the non-luminous zone of a flat flame we can, if care is taken not to distort the flame, draw down the luminous zone to a considerable extent, and if a fine platinum gauze screen be placed on each side of the lower portion of the non-luminous zone it acts in the same way as regeneration does, and gives a considerable increase in luminous surface.

Another way in which the non-luminous and non-effective portion of the flame may be reduced is by increasing the rate of combustion at the bottom of the flame.

Ten years ago Sir James Douglass introduced his multiple Argand, in which a number of circular flames burnt one within the other, whilst a series of deflectors caused a sharp current of air to impinge upon the outer flames at their base, causing a very great increase in the illuminating effect produced per cubic foot of gas consumed. In this burner the outer layers of flame were sacrificed to create an intensity of temperature which should perfect the light-giving power of the interior layers, and by setting up this intense combustion at the base of the flame the service of the burner was raised to 6 candles per cubic foot of 16 candle gas.

A still better example—because more widely known—of the same thing is to be found in Mr. Sugg's London Argand, in which the metal cone round the burner plays the same part as the deflectors in the Douglass burner, although to a smaller extent, whilst the cluster burners also benefit to a certain extent by the increase of temperature that their arrangement brings about, and I cannot help thinking that if our burner makers will attack the question of improving the flat flame by thickening the flame a little and introducing a suitable form of deflector to bring a current of air against the base of the flame, we

Annual Cost of Maintaining a Light of 48-Candle Power,—say 2000 Hours' Burning.

Results of Tests under Practical Conditions.

GAS	 "Argand"	3 16-candle Lamps consuming each 5 ft. of gas per hour.	30,000 c. ft. of gas at 3/- per 1000 90/- Renewals of chimneys 3/-	93/-
	 Regenerative burner.	1 Small Lamp consuming 6 ft. per hour.	12,000 c. ft. of gas 36/- Repair of Lamp, &c. 5/-	41/-
	 "Albo-Carbon."	2 No. 2 "Bray" Burners consuming each 3½ ft. per hour, carburetted with naphthaline.	14,000 c. ft. of gas 42/- 52 lbs. of naphthalene at 3d. 13/-	55/-
	 Incandescent.	1 New Large Mantle, 48-candle power, burning 3½ ft. per hour.	7,000 c. ft. of gas 21/- Renewal of mantles, 3 at 2/6 7/6 " chimneys 1/6	30/-
PETROLEUM.	Large Lamp.	1 48-candle Lamp burning 1 gallon in 28 hours.	Oil consumed at 7d. per gal. 41/8 Chimneys, wicks, &c. 2/4	44/-
	Small Lamps.	4 12-candle Lamps each burning 1 gallon in 84 hours.	Oil consumed 55/6 Chimney, wicks, &c. 2/6	58/-
ELECTRIC .. Incandescent.		3 16-candle Lamps absorbing each 56 "Watts."	Cost of Current at 8d., per Board of Trade unit (1000 Watt-hours) 224/- Lamp Renewals, 6 at 3/6 21/-	245/-

shall soon be able to squeeze a couple of candles more service out of these trusty old servants and add an iota more cheerfulness to our gas-lit cities.

The question of how far it may be possible to go in the extraction of light from gas is a question so complex that I hesitate to even mention it this morning, but I think that many things point to the best forms of regenerative burner, having nearly reached the limits of practical possibilities, so that in conclusion it may be well to see in what other direction the development of light from coal-gas may yet extend.

The 4 per cent. or thereabouts of heavy hydrocarbons, which in the ordinary combustion of coal-gas yield the acetylene necessary for the liberation of the carbon particles which are essential for the production of luminosity, are so small in quantity as compared with the constituents which in the burning of flame merely generate heat, that the idea naturally arose of the incandescent burner, in which by admixture of air with the coal-gas before combustion, a non-luminous but hotter flame could be produced and utilised for heating various refractory materials up to incandescence, so that they, and not the carbon, should emit the light.

In burning coal-gas from an open tube the highest temperature attained is about 1100° C. = 2012° F., whilst in the more perfect combustion taking place in a flat flame 1368° C. = 2462° F. is attained; but by mixing air with the gas before combustion as in the ordinary Bunsen burner until the mixture burns with a quiet and non-luminous flame, a temperature of 1500° C. = 2732° F. is reached, whilst by increasing the quantity of air until the flame is on the point of flashing down in the tube, the temperature rises to 1630° C. = 2966° F., or nearly 300° C. hotter than the luminous flat flame, and it is this high temperature which is taken advantage of to raise the various materials used in incandescent burners to the point at which they emit the required light.

In order to gain a relative idea of the service obtained per 5 cubic feet of 16 candle gas from the various classes of burner, choosing the best of each kind for comparison, we may take it as being as follows:—

Service yielded by Various Burners per Five cubic feet of Gas an Hour.

Flat flame.	12'5
Argand ordinary	14'0
London Argand	16'0
Regenerative	52'5
Incandescent	70'0

A colleague of mine at the Royal Naval College, Prof. Lambert, has been for some time past experimenting in

his own house as to the cost of various forms of illumination on a domestic scale, and his results for actual working over a considerable period he has kindly placed at my disposal.

The only remark I have to add to this extremely interesting and useful table is that Prof. Lambert has been extremely fortunate with his incandescent mantles and chimneys, whilst the regenerative lamp employed is manifestly too small to give anything approaching its maximum results. My own experiments would lead me to say that the incandescent and regenerative burners, taking everything into consideration, are as nearly as possible equal in cost, each of them yielding the above amount of light for an expenditure of about 35/-.

In the search, moreover, for the best method of generating light from coal-gas, we must not overlook the quality of the light emitted, and we should remember that the yellow light given out in the consumption of coal-gas is eminently adapted for resting the eye wearied by the actinic rays of the daylight, and that although an intense white or bluish white light is admirably adapted for use in picture galleries and other situations where it is necessary to bring out delicate shades of colour, yet that in the living and working room such a light must in time affect the eyesight more or less. Incandescent lighting is still in its infancy, and it has yet to be discovered how to make a mantle or comb which will not deteriorate in use and which shall not be too brittle to withstand the jars of every day use.

I have in this lecture attempted to place before you a general outline of the wonderful growth of our present methods for developing light from coal-gas, and we may be well proud of the results of the work done in the past century; but is there no reverse to this picture? Has everything been done which might have been done to encourage and increase the demands for gas? The gas managers and engineers of this country may have been a little tardy in recognising new principles, but their record is a noble one, and the one error which has been made does not rest upon their shoulders. For coal-gas to take its proper place it must be supplied at the cheapest possible rate, and all statistics show us that the increase in consumption when the price of gas is low is very large indeed, and the one thing which has more than anything else kept back the gas industry has been the fixing of the illuminating value at too high a figure. If a 14-candle standard had been adopted here in London instead of a 16, an almost unbearable burden would have been taken off the gas manager's shoulders, and not one consumer in a thousand would have noticed any difference in the light; indeed, a little trouble on the part of the companies in

advising consumers as to the best forms of burner to use would probably have resulted in an absolute gain, whilst the reduction in price consequent on the doing away with need of enrichment would have given an enormous impetus to the use of gas as a domestic fuel.

ANALYSIS OF CHROMITE.

By E. WALLER and H. T. VULTÉ.

CHROMITE, the mineral source of chromium compounds used in the arts, is essentially a chromate of iron, and is represented by the formula $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The theoretical composition calculated from this basis is—

Fe_2O_3 , 32 per cent.
 Cr_2O_3 , 68 per cent.

The mineral is frequently associated with magnesia, silica, and manganese; the full list of possible constituents of the ore is that usually given for iron ores.

The chromium is usually the most important constituent, and chromic oxide alone is determined. The refractory character of chromite is well known, and many efforts have been made to perfect a scheme of separation and estimation of the chromium which would be at the same time simple and accurate.

The following methods may be recalled:—They are divided in two distinct classes: First, those making use of liquid reagents; second, those in which fusion is used. Of the first class we mention the following:—

1. Boiling with nitric acid and potassium chlorate, Storer, *Proc. Amer. Acad.*, iv. 432; Pierson, *Am. Jour. Sci.* [2], 48, 190; Pawolleck, *Ber.*, xvi., 3008. Baubigny, *Bull. Soc. Chem.*, 1884 [2], xli., 291, finds this method very satisfactory. Many others, however, have found it tedious or unsatisfactory, or both, and such has been our experience.

2. Heating with bromine water in a sealed tube at 130° — 170° C., for several days, E. F. Smith, *Am. Jour. Science* [3], xv., 198. It is obvious that the length of this operation constitutes a very serious objection.

3. Heating for several hours at 200° C. with sulphuric acid (1 part H_2O and 2 parts H_2SO_4 by weight) in a sealed tube, Mitscherlik, *Jour. Prakt. Chem.*, 81, 108, and 83, 455.

Sulphuric acid of specific gravity 1.34 was found by Philips, *Fres. Zeits.*, xii., 189, to give the best results. The time required for this operation is about ten hours. Serious objections may be urged against these methods, both from length of time required and danger of explosion. Of the second class, or fusion methods, we find:—

1. Acid potassium fluoride, Gibbs, *Fres. Zeits.*, iii., 328, also Dubois, *Fres. Zeits.*, iii., 401; these chemists use four to five times the weight of ore in flux, and fuse from ten to fifteen minutes.

2. Alkaline or alkaline earth fluoride in conjunction with alkaline bisulphate, Sill, *Jour. Lond. Chem. Soc.*, xxxv., 292; Clarke, *Am. Jour. Science*, 1868, 173; Hagen, *Untersuchungen*, i., 163. The use of fluorides require special management to avoid the subsequent destruction of glass-ware, and involves more manipulation and skill than is required by some of the other methods.

3. Potassium bisulphate alone, Reinhardt, *Chem. Zeit.*, xiii., 430. This method is not efficient unless extraordinary precautions are taken in pulverising the ore.

4. Potassium bisulphate followed by potassium chlorate and sodium carbonate, O'Neill, *CHEM. NEWS*, 1862, 199.

5. Potassium bisulphate followed by potassium nitrate and sodium carbonate, Oudesluys, *CHEM. NEWS*, 1862, 254. Hunt, *Amer. Jour. Sci.* [2], v., 418, adds a little alkaline nitrate towards the end of the operation.

6. Caustic alkali with or without the addition of lime, Pellet, *Berg. u. Huttenman Ztg.*, xl., 224; Christomanos, *Ber.*, x., 10, substitutes magnesia for lime. Morse and Day, *Amer. Chem. Jour.*, iii., 163, advocate the use of an iron crucible.

7. Caustic or carbonated alkali in conjunction with an oxidising agent. Potassium chlorate is recommended by Schwartz, *Annalen*, lxi., 212, and Blodgett-Britton, *CHEM. NEWS*, xxi., 266. Alkaline nitrate is recommended by Calvert, *Jour. Lond. Chem. Soc.*, v., 194; Peligot, *Comptes Rendus*, 67, 871; Clouet, *Comptes Rendus*, 67, 762. Barium dioxide is recommended by Donath, *Ding. Polyt. Jour.*, cclxiii., 245; Kinnicut and Paterson, *Jour. Anal. Chem.*, iii., 132.

8. Alkaline carbonates with borax, Dittmar, *Ding. Polyt. Jour.*, ccxxi., 450, and iron, January, 1876, p. 131. The flux is composed of three parts of a mixture of potassium and sodium carbonates with two parts of borax glass.

9. Alkaline carbonate with some borax and alkaline nitrate, P. Hart, *Jour. Prakt. Chem.*, lxvii., 320.

The wet methods and those by fusion with fluoride have already been briefly discussed. Fusing alkaline bisulphate, in our experience, does not readily decompose chromite unless it is in a state of subdivision not easily obtained. Elutriation is not a desirable method of obtaining the necessary state of comminution, since the chromite possesses such a high specific gravity (about 4.5) that by elutriation a partial separation of that mineral from its associated minerals in any given sample will result, tending to produce incorrect results.

Fusion with caustic alkalis requires the use of a silver or iron crucible. Such crucibles need to be thick as compared with those of platinum, and consequently require the application of a higher heat to keep the melt at the proper temperature during fusion. Moreover, if oxidising agents are used in these crucibles they deteriorate rapidly.

Of course, where alkaline fluxes only are used, the decomposition is effected by the oxidation of the chromium to chromic acid and its union with the alkali. The presence of an excess of base, with a plentiful access of the oxygen of the air, favours such a change, and indeed is the method utilised in the manufacture of chromium salts from the ore.

The following process based on such a fusion with subsequent special treatment has been found to give satisfaction, and is thought to be more simple, accurate, and rapid than any method heretofore proposed. The plan of procedure is:—

a. Fuse 0.5 to 1 grm. with five or six times its weight of Dittmar's flux in a platinum dish.

b. Dissolve in water, filter, and evaporate, adding a little ammonium nitrate from time to time, until the last addition fails to give any odour of ammonia on heating the solution. Continue the evaporation to dryness, moisten with a few drops of nitric acid, and heat until dry.

c. Take up with water containing a few drops of nitric acid, add hydrochloric acid and sulphurous acid, or a little ammonium sulphite, boiling until the excess of SO_2 .

d. Neutralise with ammonia and boil, adding a little ammonium sulphide. Re-dissolve in hydrochloric acid, and re-precipitate as before to purify the precipitate. Ignite and weigh Cr_2O_3 .

Comments.—a. The flux is made by fusing together two parts of borax glass with three parts of (dry) sodium and potassium carbonates, mixed approximately in proportion of their molecular weights (106 to 138). After fusing the mixture is poured out upon a cold surface (a dry platinum dish floated on the surface of cold water), and then coarsely powdered for use. As it is somewhat hygroscopic, it should be kept in a tightly corked bottle. The borax makes the flux somewhat pasty, so that it holds the mineral partly in suspension, and thus favours the decomposition. A convenient form of dish for the fusion is one about 2 inches in diameter, and half an inch deep, with rounded bottom, and provided with a small ear for grasping with the tongs. If a shallow dish of the kind is not available, the convexity of the cover of a large fusion crucible makes a very good substitute. The flux has

practically no effect upon the platinum. Over three hours of fusion caused in one case a loss of 3.5 m.grms. and ordinarily little or nothing.

A good way of managing the fusion is first to melt in the dish the requisite quantity of flux, and then allow it to cool; then weigh out the finely pulverised ore, and, by means of a feather, brush it on to the surface of the melt, spreading it as evenly as possible.

Then fuse with a good Bunsen burner, stirring occasionally with a platinum wire, until the decomposition is apparently complete. This is likely to require not over forty minutes, if the ore has been well pulverised and the stirring has been sufficiently frequent. If either point has been neglected it may require longer. Remove the heat temporarily, and, as the mass cools, stir with the platinum wire in such a way as to take a portion of the material from the bottom of the melt. As soon as this hardens sufficiently, withdraw and examine it for black grains of undecomposed ore. If any are seen, replace the test bead in the dish, cover, and apply the heat. The material soon melts off from the wire, when the cover may be removed, unless the heat is insufficient to keep the mass fluid without its use. When decomposition is apparently complete, remove the heat and allow the mass to cool.

b. The portion soluble in water, besides the excess of the constituents of the flux, should contain all of the chromium as alkaline chromate, together with some alkaline manganate, aluminate, and silicate. That insoluble in water should dissolve completely in hot dilute hydrochloric acid. If some black grains of undecomposed ore remain, they must be filtered off and fused with a little more of the flux, as in the first instance.

The evaporation of the water solution, with addition of ammonium nitrate (Genth, CHEM. NEWS, vi., 32), cause the manganese to separate as insoluble MnO_2 , the alumina being at the same time precipitated as hydrate, which, by the prolonged heating, assumes a form practically insoluble in nitric acid, especially when hot. The last addition of nitric acid and heating will render all the silica insoluble, so that eventually nothing soluble remains except alkaline chromate and nitrate.

c. The object of this step is simply to reduce the chromium to the form of base. The presence of hydrochloric acid is of advantage in the next step, as it affords ammonium chloride, which favours the separation of chromium hydrate.

d. It may be found that at first no precipitate appears on neutralising with ammonia. On boiling, however, to remove the slight excess of ammonia, chromium hydrate separates. The addition of a little ammonium sulphide favours the separation. The precipitate produced in presence of the fixed alkalis is, however, never sufficiently pure to be at once ignited and weighed. After washing it requires at least one re-solution in hydrochloric acid and re-precipitation in the same manner as before. A third re-precipitation may be advisable.

If alkaline salts remain with the precipitate, the error involved is not only due to the additional weight of those contaminants, but they may induce a further increase in weight due to the partial formation of alkaline chromate.

List of analyses made by the preceding method:—

	Cr ₂ O ₃ found per cent.	Cr ₂ O ₃ calc. per cent.
1. Chromite and iron ore ..	4.18	4.38
2. " " ..	2.92	2.80
3. " " ..	3.87	3.96
4. " " ..	2.75	2.64
5. " " ..	2.57	2.72
6. " " ..	2.98	2.88
7. " " ..	4.44	4.32
8. " " ..	4.027	4.07
9. " " ..	8.44	8.64
10. " " ..	3.52	3.51
11. " " ..	2.77	2.907
12. " " ..	10.57	10.60

These samples were made from a chromite mixed with iron and manganese ores. The chromite was found to contain 57.00 and 57.025 per cent of chromic oxide as a result of determination by different analysts.—*School of Mines Quarterly*, xiii., No. 3.

THE OFFICIAL METHOD FOR THE ANALYSIS OF NON-STARCHY FOODS (COARSE FODDERS, OIL SEEDS, AND OTHER RESIDUES) FOR 1890—91.

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Preparation of the Sample.

THE substance is to be ground until all of it will pass through a sieve with circular holes 1 m.m. in diameter.

Hygroscopic Water.

Dry 2 to 3 grms. of the substance for four hours, heated fully to the temperature of boiling water, in a current of dry hydrogen, but without allowing the glass containing it to come in contact with the boiling water.

Ash.

Char the substance at a low red heat, which is conveniently done in a Fletcher gas muffle furnace, heated not by the large gas burner that is supplied with the furnace, but by a Fletcher solid flame burner (No. 46b); exhaust this charred mass with water; collect the insoluble residue on a filter, burn, add this ash to the residue from the evaporation of the above aqueous extract, and heat the whole to low redness till the ash is white.

Ether Extract.

Extract 2 to 3 grms of the substance, dried as for the determination of the moisture, with anhydrous and alcohol-free ether, sixteen hours. Dry the extract by exposure to the full heat of boiling water, in a current of dry hydrogen, to constant weight.

Crude Protein.

Determine nitrogen by the Kjeldahl method as directed for nitrogen in fertilisers, and multiply the result by 6.25 for the crude protein.

Albumenoid Nitrogen.

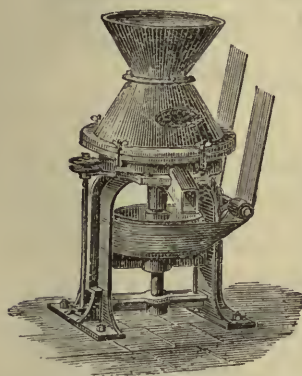
Stutzer's Method.—Prepare cupric hydrate as follows: Dissolve 100 grms. of pure cupric sulphate in 5 litres of water, and add 2.5 c.c. of glycerin; add dilute solution of sodium hydrate until the liquid is alkaline; filter; rub the precipitate up with water containing 5 c.c. of glycerin per litre, and then wash by decantation or filtration until the washings are no longer alkaline. Rub the precipitate up again in a mortar with water containing 10 per cent of glycerin, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per c.c. of this mixture. To 1 gm. of this substance add 100 c.c. of water in a beaker, heat to boiling, or in the case of substances rich in starch heat on the water bath ten minutes, add a quantity of cupric hydrate mixture containing 0.7 to 0.8 gm. of the hydrate, stir thoroughly, filter when cold, wash with cold water, and put the filter and its contents into the concentrated sulphuric acid for the determination of nitrogen after Kjeldahl. For the above filtration use Schleicher and Schüll's No. 589 paper, or Swedish paper, either of which contains so little nitrogen that it can be left out of account.

If the substance examined consists of seed of any kind, or residues of seeds, such as oil cake or anything else rich in alkaline phosphate, add a few c.c. of a concentrated solution of alum just before adding the cupric

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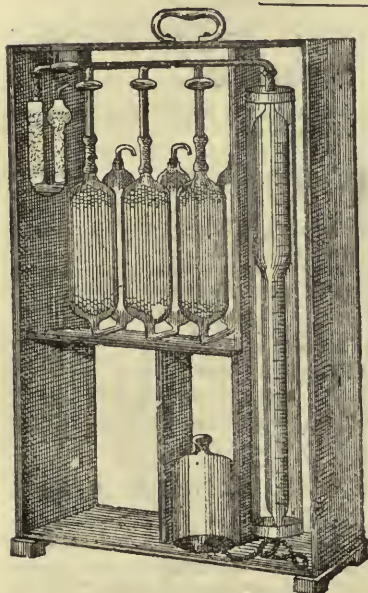
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hydrate, and mix well by stirring. This serves to decompose the alkaline phosphate. If this is not done cupric phosphate and free alkali may be formed and the protein copper may be partially dissolved in the alkaline liquid.

Crude Fibre.

Extract 2 grms. of the substance with ordinary ether, at least nearly completely, or take the residue from the determination of the ether extract. To this residue, in a 500 c.c. (Erlenmeyer) flask, add 200 c.c. of boiling 1·25 per cent sulphuric acid; connect the flask with a return-flow condenser, the tube of which passes only a short distance beyond the rubber stopper into the flask. Boil at once, and continue the boiling for thirty minutes. A blast of air conducted into the flask may serve to reduce the frothing of the liquid.

Filter, wash thoroughly with boiling water till the washings are no longer acid, rinse the substance back into the same flask with 200 c.c. of a boiling 1·25 per cent solution of sodium hydrate at least almost free from sodium carbonate, boil at once, and continue the boiling for thirty minutes in the same manner as directed above for the treatment with acid. Filter in a Gooch crucible and wash with boiling water till the washings are neutral, dry at 110° C., weigh, incinerate completely, and give the loss of weight for crude fibre.

The filter used for the first filtration may be linen, one of the forms of glass wool, and asbestos filters recommended in the last report, or any other form that secures clear and reasonably rapid filtration. The carbonate free sodium hydrate can be obtained of the Troy Laundry Machinery Company, 32, Dey Street, New York, or 297, Wabash Avenue, Chicago, under the name of "Greenbank Alkali Company," double refined 98 per cent caustic soda, it being the same as that recommended for the Kjeldahl nitrogen method. The solutions of sulphuric acid and sodium hydrate are to be made up of the specified strength accurately by titration, and not merely by the areometer.

AN IMPROVED METHOD OF DETERMINING
SMALL PERCENTAGES OF SILVER AND GOLD
IN BASE METALS, MATTES, &c.*

By CALEB WHITEHEAD,
Assayer to the Mint Bureau, Washington, D.C.

ANYONE having frequent occasion to report the values of silver and gold in such material as crude copper, copper mattes or ores, metallic iron, zinc, &c., will appreciate the advantages of a method which affords accurate results with little expenditure of time. The large production of pure copper by electrolytic methods from silver- and gold-bearing copper ores, renders some such method very desirable in view of the various transfers of,—(1), ores to the smelters; (2), mattes to the refiners; and last, the crude copper to the electrolytic refinery; each of which transfers carries a commercial charge of the bullion contents.

While the proposed method is available for a great variety of base products, it will perhaps be best illustrated by its use in determining the silver and gold contents in crude copper, or the mattes resulting from bullion-bearing copper ores. The adaptability of the method to other base metals will readily suggest itself to the experienced assayer.

Given a crude copper or matte carrying from 30 ounces of silver and 0·10 of an ounce of gold, upward, the usual method would be scorification. It is usual to take for assay from 0·05 to 0·1 assay ton to each scorifier, with which are used from 40 to 50 grms. of test-lead, one-half of which is mixed with the ore in the scorifier and the remainder used as a cover. The scorifier is now intro-

duced into a hot muffle and the door closed until the lead is melted, when it is opened, and about 1 grm. of borax glass placed on the lead. Oxidation begins at once, and the lead and base metals are rapidly scorified off until the slag covers the metal, when the assay is poured into a mould. If the lead button still retains much copper, or is hard or brittle, it is again scorified, with the addition of more test-lead if necessary. When the lead button is soft and of proper size, it is cupelled and the button weighed and parted. Several scorifications are sometimes necessary before the button is ready for the cupel.

The two objections to this method are, first, the loss of silver during scorification and cupellation, the latter due chiefly to the copper remaining in the lead, which it is practically impossible to remove in the scorifier, and which takes silver into the cupel. These losses I found to amount to from 2·33 to 2·78 per cent of the silver present in the copper. My experiments were made with pure copper and pure silver, the silver being added in the proportion of 100 ounces per ton of alloy.

The second objection is the small amount of bullion which can be operated upon, which necessitates the use of many scorifiers where small amounts of gold are to be estimated, which is usually the case.

To avoid the doubtful results of scorification processes the following method has been adopted at the copper works of a firm having large interests at stake:—

One assay ton of copper is dissolved in nitric acid, diluted, and allowed 24 hours to settle. The solution is now filtered from the slight sediment containing the gold. A few drops of hydrochloric acid are added to the filtrate and the solution again allowed 24 hours for silver chloride to deposit, when it is filtered, washed, and the two filters dried, combined, scorified with test-lead, and cupelled. The chief objections to this are—(1), the time required; (2), the small amount of precipitate obtained and the danger of loss in scorifying silver chloride; (3), the greater solubility of silver chloride as compared with the bromide.

While the method used at these works is an advance over previous practice, yet the time employed and the uncertainties indicated leave much to be desired. The protracted time allowed for settling is necessitated by the exceedingly fine condition of the gold resulting from the solution of a metal carrying possibly from 0·10 to 5 ounces of gold per ton of metal. It would pass through a filter unless allowed to aggregate by standing.

The larger quantity (say 100 ounces) of silver per ton will give but a slowly subsiding cloud (impossible to filter) when newly precipitated as chloride. The scorification of these combined precipitates, one of them being silver chloride, cannot give results quite satisfactory, despite the time involved, some 48 hours at least.

The method which I will now briefly describe was devised to meet just such cases, and is suitable for the bullion valuation of zinc, iron, nickel, &c., as well as the sulphides and arsenides of iron and copper. To illustrate the proposed method, which has been found effective and useful, the treatment is detailed for a crude metallic copper carrying both silver and gold. It will be understood that sodium bromide is chosen as a precipitant because of the greater insolubility of silver bromide over the chloride, and also that the soluble lead salt is added in order that the heavy precipitate of lead bromide may envelop and promptly carry down the silver bromide cloud, which otherwise would require long waiting for its subsidence, as well as to furnish the lead necessary for cupellation.

Weigh out from one to four a. t., depending upon its richness, place it in a beaker of 500 c.c. capacity, and add gradually enough nitric acid to dissolve it completely, heat until red fumes cease to come off, dilute with water, and add 50 grms. of lead acetate, stir, and when dissolved add 1 c.c. dilute sulphuric acid, and allow the lead sulphate to settle. Filter into a 1000 c.c. flask, and fill to the mark with distilled water.

* Read at the Chemical Section of the Franklin Institute, May 17th, 1892.

The filter contains the gold which has been collected and carried down by the sulphate of lead. The filter-paper and precipitate are dried, the paper burned, and the ash and lead sulphate scorified with test-lead. The button is cupelled and the gold, with any trace of silver it may contain, is weighed. Add silver and part the gold in the usual way. Note the amount, if any, of silver found, and include the proper proportion of the amount with that found in the solutions as about to be described.

In order that there may be a control assay, the solution is divided into two equal parts, to each of which a saturated solution of sodium bromide is added with constant stirring as long as a precipitate is produced. The precipitates settle quickly and filter and wash well. Cold water only should be used, and the washing be continued until the washings are free from copper. Any bromide of lead dissolved during the washing may be neglected, as I have never found it to contain more than a trace of silver, even when assaying ores carrying many thousand ounces.

The precipitate when dry can be brushed from the paper without difficulty, and thus the trouble of burning the filter is avoided. The bromides are now mixed with three times their weight of carbonate of soda and a small amount of flour or other reducing agent placed in a small crucible covered with borax glass and melted down in the muffle. The button should weigh about 2 grms. and be free from copper and other injurious impurities. This button is cupelled at a low temperature, so that the cupel "feathers" nicely. The time required is from three to five minutes. Duplicate assays usually agree within two-tenths of an ounce per ton.

The following examples are from copper bullion:—

	Silver Ounces.	Ounces.	Gold. Ounces.
No. 1	61'30	61'20	0'10
No. 2	63'45	63'30	0'17

Had the gold button contained silver, one-half of its silver contents would have been added to the silver recovered from the solutions, since the gold is estimated on the whole weight, while two determinations of silver are made on the same weight.

The following is an example from a silver-bearing cast iron from the U.S. Mint at Philadelphia. It was dissolved in nitric acid, diluted, and precipitated with lead and sodium bromide. After washing, the bromides were dried and brushed from the filter. No. 1 was mixed with 10 grms. of litharge, a little flour, the usual amount of soda, and covered with borax. Melted down and cupelled the button gave 30'80 ounces per ton. No. 2 was mixed with test lead and borax, and scorified. It gave 29'90 ounces per ton, 0'90 of an ounce less than No. 1. However, this would be considered a very close agreement by the old method.

The following is an ore from Colorado, very base and with a gangue of sulphate of barium. It proved very unsatisfactory to assay by scorification, duplicates not agreeing at all. The ore was treated with nitric acid and filtered, the residue being assayed separately.

The following are my results:—

	No. 1. Ounces.	No. 2. Ounces.
Residues	32'50	35'95
Solutions	454'90	453'30
As a total	487'40	489'25
Difference of	1'80	—

Gold was not separated in the residues. The highest assay gotten by scorification was about 467 ounces, which shows 20 ounces in favour of the new method, with a reasonably close agreement in different assays.

Pipettes for Hydrofluoric Acid.—G. P. Vannier (*Journal of Analytical Chemistry*).—These instruments are constructed of ceresine, which is not attacked by hydrofluoric acid.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 9.)

II.—SYNTHESIS OF CUPRIC SULPHATE.

PARALLEL with the experiments which have just been described was commenced a series of syntheses of cupric sulphate. It was hoped that the results might furnish a valuable confirmation to the conclusions based upon the analytical work, but the outcome of the series was very disappointing.

The method of experiment was as follows:—A weighed amount of pure electrolytic copper (for mode of preparation, see *Proc. Amer. Acad. Arts Sci.*, xxv., 199, 206), which had been ignited in hydrogen, was dissolved in the purest nitric acid in a platinum flask provided with bulb tubes for the condensation of spray. A slight excess of pure sulphuric acid was then added, and the whole was evaporated to small bulk in a platinum dish. After transferring to a small crucible enclosed in a larger one, the remaining solution was evaporated to dryness on the steam bath; and the residue was gradually raised to a temperature of 400°. After some time the crucible was quickly covered, placed in a phosphoric oxide desiccator, and allowed to cool in a vacuum. Air having been admitted through suitable drying tubes, the crucible was quickly weighed. The product of the experiment soon reached constant weight upon re-heating, but it was invariably found to contain a very perceptible amount of imprisoned sulphuric acid, which rendered its solution strongly acid to methyl orange. It is evident from the preceding section that this impurity is not retained when pure sulphuric acid is added to powdered cupric sulphate which has already been nearly dehydrated, but only when the salt is crystallised from strongly acid solutions. This fact rendered the present experiments useless for their original purpose. The results of the two determinations show how insidious constant error may be, if not guarded against by check experiments.

Synthesis of Cupric Sulphate from Metallic Copper.

(Weights reduced to vacuum. Sp. gr. of Cu = 8'95; of CuSO₄ (Hampe and Karsten) = 3'61.)

No. of experiment.	Metallic copper taken. Grms.	Cupric sulphate found. Grms.	Per cent of copper in cupric sulphate.
40.	0'67720	1'7021	39'786
41.	1'00613	2'5292	39'781
Average			39'784
From analysis of cupric sulphate dried at 400°			39'807

In order to show that the large difference between these two averages was due solely to the occlusion of sulphuric acid, the following experiment (No. 42) was made:—3'1227 grms. (in vacuum) of the purest crystallised cupric sulphate were dried at 400°, the residue weighing 1'9963 grms. The nearly anhydrous salt was then carefully dissolved in water, and after the addition of small quantities of nitric and sulphuric acids it was evaporated and ignited at a temperature even somewhat higher than before. A gain of 0'0013 gm. was apparent, very nearly corresponding to the difference noted above. The acids, tested immediately afterwards, left no weighable residue upon evaporation.

While it was apparent that these experiments were useless for their original purpose, it was hoped that their comparison with similar syntheses from cupric oxide might furnish valuable indirect evidence with regard to

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

the quantitative relations of the latter important substance. The hope was not in vain.

The cupric oxide used as the basis of the three following experiments was prepared essentially in the manner described in *Proc. Amer. Acad. Arts Sci.*, xxv., p. 199. The three experiments represent as many different preparations, in making which various different precautions were observed; but in a paper already far too prolix the omission of these minor points will be well pardoned. The cupric oxide was ignited to constant weight at a dull red heat in a double crucible, and cooled in a vacuum as usual. The outside crucible was of platinum in the second and third experiments, and in these cases the inner crucible was observed to have gained noticeably in weight during the ignition. The last weight was adopted, for obvious reasons. In the first and last cases the solution of the oxide was conducted in the crucible, without transferring, while in the second experiment the cupric oxide was dissolved in the platinum flask with bulb tubes. In each case both nitric and sulphuric acids were added, that the conditions might be similar to those of the preceding syntheses. The cupric sulphate used by Baubigny in his analyses was prepared in a somewhat similar way, and hence in this respect his result is comparable with these.

Synthesis of Cupric Sulphate from Cupric Oxide.

Weights reduced to vacuum. Sp. gr. of CuO = 6.3; of CuSO₄ = 3.61.

No. of experiment.	Cupric oxide taken. Grms.	Cupric sulphate found. Grms.	Per cent cupric oxide in cupric sulphate.
43.	1.0084	2.0235	49.835
44.	2.7292	5.4770	49.830
45.	1.0144	2.0350	49.848
Average			49.838
Theory if Cu = 63.6			49.856
" " = 63.34			49.774
Baubigny's result			49.815

The comparatively close agreement between the average and the theory is solely due to an elimination of opposite errors. This fact will be more evident in the following section.

In order to show that no material was mechanically lost during the syntheses, the last sample of cupric sulphate from each of the two series was electrolysed. The result of one of these electrolyses has already been given in Experiment 16; the other yielded 0.8096 gm. of metal from 2.0350 grms. of the sulphate, or 39.78 per cent of copper.

It is evident that impure cupric sulphate prepared in this manner contains about 39.784 per cent of copper and about 49.838 per cent of ordinary cupric oxide. That is to say, 39.784 parts of copper correspond to 10.054 parts of the remainder of cupric oxide. Assuming this remainder to consist solely of oxygen, the atomic weight of copper would be 63.312. But upon comparing the quantity 10.054 with the quantity of sulphuric anhydride found by difference, 50.162, it is evident that a grave error exists in the former figure. This error becomes only more apparent when allowance is made for the occluded acid.

These inferences are based upon data of somewhat uncertain accuracy, it is true; but the error is nevertheless so large as to be apparent even to cruder analysis than this. The full explanation of the results, as well as of the variation exhibited by Baubigny's analysis, must be deferred to the next section. The doubts raised by the data under discussion formed a useful introduction to the study of cupric oxide.

(To be continued.)

Prevention of Bumping in Boiling.—E. Pieszczyk (*Chemiker Zeitung*).—The author suspends in the liquid to be boiled a glass tube, closed above, 5–8 c.m. long and 5–10 c.m. in width.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, June 24th, 1892.

Prof. A. W. RÜCKER, F.R.S., in the Chair.

THE following communications were made "*On Breath Figures*," by Mr. W. B. CROFT.

After mentioning the observations of early experimenters on the subject, the author described a method which he found to give the best result. A coin is placed on a glass plate for insulation. Another glass plate which is to receive the impression is well polished and laid on the coin, whilst a second coin is placed above the first. The coins are put in connection with the poles of an electrical machine, giving one inch sparks for two minutes. When the coins are removed and the glass breathed on, clear frosted pictures of the coins are seen on the glass. The microscope shows that moisture is deposited on the whole surface, the size of the minute water granulation increasing, as the part of the picture is darker in shade. The thickness of the glass seemed to make no difference, to the result, and several plates and coins might be piled up alternately. If carefully protected time appears to have little effect on the figures, but they can be removed by rubbing whilst the glass is moist. Failures and their causes were discussed, and the more complex phenomena produced by strong discharges described. It was also pointed out that breath figures could be produced by laying a coin on a freshly split surface of mica, and that a coin laid on glass for some time leaves its traces. Perfect reproductions of printed matter have been obtained by placing a paper printed on one side only between two sheets of glass for ten hours. Some substances such as silk, in contact with glass, give white figures, whilst wool, cotton, &c., give black ones. Various analogous effects are noticed in the paper, and the several views put forward in explanation of the phenomena examined.

A communication on the same subject from the Rev. F. J. SMITH, was read by Prof. Perry. He had investigated some of the effects, and had succeeded in photographing the impressions, prints from which were shown. He had also examined the influence of various gases on the result, and found that oxygen gave the best figures. In a vacuum no figures could be obtained. The effect of temperature had also been tested.

Prof. S. P. THOMPSON said details of early researches were given in *Poggendorff's Annalen* for 1842. It was there pointed out that better results were obtained by putting a spark gap between the coin and the machine. Since the effects did not depend on the way in which the sparks passed, he thought it was probable that electrical oscillations were involved. He himself had worked at the subject in 1881, and recently repeated some of the experiments. Figures could be produced on almost any polished surface. He got best results by using a small induction coil giving about 3 m.m. spark for about five seconds. In 1881 he accidentally noticed that photographs could be got on ebonite. Hot coins put on uncleaned glass gave good breath figures.

A MEMBER said that instead of breathing on the plates he and Mr. Garrett had sifted finely powdered red lead over them to get the figures. They had also fixed the figures by etching with hydrofluoric acid.

Mr. CROFT exhibited some figures he obtained two years ago which were still quite distinct.

"*On the Measurement of the Internal Resistance of Cells*," by Mr. E. WYTHE SMITH.

After referring to the methods hitherto used, the author explained a modification of Mancès' test which he had recently devised. One pole of the battery to be tested is connected to the similar poles of two other batteries. Each battery has a separate circuit, through which

currents are allowed to pass. Selecting a point A at the opposite pole of the battery to be tested, points B and C in the circuits of the auxiliary batteries are found whose potentials are equal to that of A. The resistances between each pair of points, AB, AC, BC, are then measured by a Wheatstone bridge. Calling these resistances R_1 , R_2 , and R_3 respectively, it is shown that the internal resistance required is given by the formula—

$$b = \pi + \frac{\pi^2}{r} + \frac{\pi^2}{r^2} + \&c., \text{ where } \pi = \frac{R_1 + R_2 - R_3}{2},$$

and r is the external resistance of the circuit containing the battery tested. For an accumulator discharging $b = \pi$ to within about 2 per cent.

Prof. PERRY inquired how far the results obtained agreed with those got by the older methods, and whether they depended on the time the keys were kept down. In the old methods it was assumed that an instantaneous rise in P.D. occurred on breaking the circuit. This might or might not be true. He was inclined to regard the P.D. and current as functions both of resistance and time. The behaviour of cells seemed to indicate the existence of something like capacity, or rather, capacities and resistances in series.

Prof. AYRTON said the paper was of great interest, for it made possible what could not be done before, viz., to find the resistance of a cell without appreciably altering the current through it. Although the new method required more cells this was not prohibitive, for the result sought was of considerable scientific importance. The same method was applicable for finding the resistance of dynamo armatures when working, a quantity which had hitherto been unattainable by direct measurement.

Mr. LANE FOX said the perplexing changes in the P.D. of secondary cells were to be accounted for by changes in the electrolyte which occurred in the pores of the plates. He could detect no flaw in the reasoning given in the paper.

Dr. SUMPNER remarked that the method was a valuable one, for it depended on bridge tests, which could be made with considerable accuracy. On the other hand, it was a false zero method, and therefore liable to errors arising from changes of this zero.

Prof. AYRTON pointed out that these errors could be eliminated by reversing the bridge battery.

Mr. RIMINGTON said although the testing currents were small they might affect the E.M.F., and thus introduce an error in b . This could be tested by using alternate currents and a telephone.

In reply to Prof. Perry, Mr. SMITH said the results agreed with those obtained by the older methods to within the limits of accuracy obtainable by the latter methods; this might amount to something like 15 per cent.

"On the Relation of the Dimensions of Physical Quantities to Directions in Space," by Mr. W. WILLIAMS.

In February, 1889, Prof. RÜCKER recalled attention to the fact that in the ordinary dimensional formulæ for electrical quantities the dimensions of μ (permeability) and k (specific inductive capacity) are suppressed. In the discussion on that paper Prof. S. P. THOMPSON pointed out that lengths should be considered as having direction as well as magnitude, for if so regarded, difficulties arising from different units, such as *couple* and *work*, having the same dimensions would be avoided. Developing this idea, the author takes three mutually perpendicular lines, along which lengths are measured. Calling unit lengths along these lines X, Y, and Z respectively, the various dynamical units, such as velocity, acceleration, force, work, &c., are expressed in terms of M, T, X, Y, and Z. The formulæ then denote the directional as well as the numerical relations between the units, and the dimensional formulæ are therefore regarded as the symbolical expressions of the physical nature of the quantities, so far as they depend on lengths, mass, and time. In this system areas and volumes are represented by products of different vector lengths, instead of

by powers of a single length, and angles and angular displacements by quotients of rectangular vectors, instead of being pure numbers. For physical purposes pure numbers may be defined as ratios of concretes of the same kind similarly directed (if directed at all). A plane angle has dimensions $X^{-1}Y$, X being in the direction of the radius, and Y that of the arc, whilst solid angles have dimensions YZX^{-2} and radii of curvature Y^2X^{-1} . It is also shown that π is a concrete quantity of the dimensions either of plane or of solid angle. This is of considerable importance in connection with the radial and circular fluxes in the electromagnetic field.

In deducing the dimensional formulæ for electrical and magnetic units, the rational and simplified relations given by Mr. Oliver Heaviside in the *Electrician* of October 16 and 30, 1891, are used. Instantaneous axes are taken at any point of an isotropic medium (the ether), such that X coincides with the electrical displacements, Y with that of the magnetic displacement, and Z with the intersection of the two equipotential surfaces at that point.

Starting with the relation $\mu H = \text{energy per unit volume}$, the formulæ for the various quantities in terms of μ are obtained. These simplify down to those of the ordinary electromagnetic system by putting $\mu = 1$ and suppressing the distinction between X, Y, and Z. Similarly commencing with $k E^2 = \text{energy per unit volume}$, formulæ in terms of k are obtained which, when simplified as above, give those of the ordinary electrostatic system. Examples of the consistent way in which the results work out are given in the paper, and the whole subject is discussed in detail both by Cartesian and vectorial methods.

The formulæ in terms of μ and k are used to trace out and examine the various analogies between electromagnetism and dynamics, thereby obtaining a connected dynamical theory of electromagnetism. Inquiry is then made to what dimensions of μ and k in terms of M, T, X, Y, Z, render the interpretation of electrical and magnetic units simple, natural, and intelligible as a whole. The conditions imposed (for reasons stated in the paper) are, firstly, that the dimensions of μ and k satisfy the relation $[\mu k] = Z^2 T^{-2}$; secondly, that the powers of the fundamental units in the dimensional formulæ shall not be higher or lower than those found in the formulæ of the ordinary dynamical quantities; and thirdly, that quantities which are scalar or directed must also be scalar or directed when their dimensions are expressed absolutely. Subject to these conditions it is shown that the possible dimensional values of μ and k are eight in number. Of these only two lead to intelligible results. These are (1) $\mu = M(XYZ)^{-1}$ and $k = M^{-1}XYZ^{-1}T^2$, and (2) $\mu = M^{-1}XYZ^{-1}T^2$ and $k = M(XYZ)^{-1}$. According to (1) μ is the density of the medium, electrical energy is potential, and magnetic energy kinetic. By (2) k is the density of the medium, electrical energy is kinetic, and magnetic energy potential. Full interpretations of the dimensional formulæ of all the electromagnetic quantities as obtained in accordance with the above conditions are given in the paper.

Prof. S. P. THOMPSON said the paper was a very important one, and thought the idea of finding dimensions for μ and k , which would rationalise the ordinary dimensional formula, a great step. The use of vectors was a valuable feature, whilst the employment of X, Y, and Z, instead of L, removed many difficulties connected with dimensional formulæ. Other difficulties might be cleared up by paying attention to the signs of the vector products and quotients, and to the order in which the symbols were written. Another important matter was the use of Mr. Heaviside's "rational units,"—a system which merited serious attention. In conclusion, Prof. THOMPSON expressed a hope that in accordance with the resolution of the Electrical Congress at Frankfort, both permeability and specific inductive capacity should be designated by Greek symbols.

Prof. O. HENRICI expressed his admiration of the way in which the subject had been treated in the paper. He

had long held that clear ideas of physical quantities were best got by vectorial methods. He also congratulated the author on his treatment of plane and solid angles as concrete quantities.

In a communication addressed to the Secretaries, Prof. O. J. LODGE remarked that physicists in England were more or less familiar with the advantages of retaining μ and k in dimensional expressions before Prof. Rücker's paper of February, 1889, brought the matter closely home to students. The system of mechanical dimensions suggested for electrical quantities in an appendix to "Modern Views of Electricity" was not put forth as the only one possible, but as one having certain probabilities of truth in its favour.

Prof. RÜCKER said that although Mr. Williams and himself had talked over certain minor points in the paper the main ideas brought forward were quite original, having been fully developed by Mr. Williams before the author mentioned the subject to him (Prof. Rücker).

A paper on "*Molecular Forces*," by Mr. W. SUTHERLAND, communicated by Prof. CAREY FOSTER, was taken as read.

The CHAIRMAN announced that both this paper and that of Mr. Williams would be printed in the *Phil. Mag.* during the long vacation, so that they could be fully discussed early next session.

NOTICES OF BOOKS.

Year-Book of Chemistry. Report on the Most Important Advances in Pure and Applied Chemistry. ("Jahrbuch der Chemie." Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie). Edited by RICH. MEYER. Vol. I., 1891. Frankfurt-on-Maine: Bechhold, 1892.

THE Editor points out in his preface that the increase of specialism renders it from day to day more difficult for the student or expert to remain in touch with the general course of discovery and improvement, even in his own peculiar department, much less in the other spheres of chemical research.

We certainly find in not a few scientific journals periodical sketches of the most important results. But these summaries form no complete whole; they are scattered in the periodical literature of the day, and not without a very serious expenditure of time can any experimentalist venture to say that he has seen everything which has been done in connection with any given subject. The evil increases since original work has begun to appear not only in the so-called "languages of culture," but in Bohemian, Polish, Russian, Roumanian, &c. Hence there arise unedifying disputes as to priority, as well as waste of time and trouble, when one chemist takes up a question which, unknown to him, has already been entered upon and perhaps decided. Thus we may welcome a work like the present, which in every year will summarise all the most important chemical work effected in the preceding season.

The editor has secured the co-operation of Professor Dr. H. Beckurts, of Brunswick, for pharmacy and the chemistry of foods and articles of personal consumption; Prof. Dr. R. Benedikt, of Vienna, for the technology of fatty matters; Prof. Dr. C. A. Bischoff, of Riga, for organic chemistry; Prof. E. F. Dürre, of Aix-la-Chapelle, in metallurgy; Prof. J. M. Eder and E. Valenta, of Vienna, in photography; Prof. C. Häussermann, of Stuttgart, for inorganic chemical technology and explosives; Prof. Dr. G. Krüss, of Munich, for inorganic chemistry; Professors Maercker and Böhling, for agricultural chemistry, the technology of the carbohydrates, and the industries of fermentation; Prof. R. Meyer, of Brunswick, for the chemistry of coal tar and colouring matters; Prof. Dr. W.

Nernst, of Göttingen, in physical chemistry; and Dr. F. Röhm, of Breslau, in physiological chemistry.

There is a good opening for a work entrusted to such hands, and we wish it full success.

Catalogue of Chemical Apparatus and Pure Chemicals sold by Townson and Mercer, 89, Bishopsgate Street Within, London, E.C., Wholesale and Export Dealers in Chemical and Scientific Apparatus and Pure Chemicals.

If we compare this catalogue in its present form with the earlier editions we shall see that the enterprising firm in question have made those additions which recent advance in chemical and physical science require. Thus we find here a duly priced list of the appliances for the cultivation and study of microbia, such as sterilising ovens, cultivating troughs, serum inspirators, sterilisers, digesters, incubators, gas regulators, counting apparatus, &c., of the best and most modern constructions, to suit all the requirements of the bacteriologist.

Spectroscopes of different makes and prices now figure quite prominently among the requisites of the analyst and experimentalist. Lovibond's "tintometer" is mentioned as a valuable apparatus for measuring and recording colours, especially for dyers and tissue printers.

Apparatus for gas analysis is supplied in considerable variety according to the designs of Lunge, Orsat Muencke, Winkler-Hempel, Staedel, Elliott, and others.

In addition to apparatus required in the chemical laboratory, we find here assortments of the appliances required in the study of pneumatics, heat, light, crystallography, acoustics, electricity in all its branches, mechanics.

There are lists of the sets of apparatus recommended by the Science and Art Department, Prof. Wanklyn's sets of apparatus and reagents for the analysis of water and milk; Dr. Graham's set for the analysis of malt, beer, &c.; blowpipe apparatus; sets for the Oxford and Cambridge local examinations; for the diploma of public health; the pharmaceutical set, &c. There is a full and illustrated notice of the devices of Messrs. Fletcher and Co. for the production and application of heat.

In short, the student, the experimentalist, and the manufacturer will find this catalogue a useful guide to the apparatus which they may require for any purpose.

The Chemical Constitution of some Colonial Fodder Plants and Woods. By CHARLES F. JURITZ, M.A., Fellow of the University of the Cape of Good Hope. Wynberg: Wynberg Times Office, 1892.

THIS little book is a step in a direction which is at once very useful and too much neglected. The University of the Cape of Good Hope has, it appears, offered "Fellowships" to graduates on certain conditions. One of these is that: "The holder shall for a term of years devote himself to the study of a definite branch of literature or of science of direct interest to South Africa, such as the ethnology and languages of the native races, the botany or zoology of South Africa, or the chemistry of South African plants and minerals." The author selected the chemistry of South African woods, fodders, and leguminous plants—a subject of great importance, both scientific and practical, and at the same time hitherto much neglected.

He shows the influence of climate on the albuminous constituents of plants which are relatively more abundant in a warm than in a cold climate. The plants grown in the warmer locality of Oudtshoorn contain more albumen than those grown at Stellenbosch, and the latter, again, are richer in albumen than those grown in Europe. An important consideration in comparing South African plants with those of Europe is that the former always

contain a smaller proportion of water; consequently their valuable constituents are relatively larger in proportion. This point comes into special prominence in the various products used for the food of cattle.

As regards tannin, none of the African woods and barks seem to equal those of Australia, though they exceed those of Europe. The richest, the bark of "beukenhout," contains 15.96 per cent of tannin. By an oversight, the trees are tabulated only by their Caffir or Cape-Dutch names; the botanical names should have been given for identification. Another oversight is that mahogany, acacia, *Abies canadensis*, and *Quercus castanea*, are given as European.

The author's pamphlet is not merely useful in itself, but forms a good example which we hope to see largely followed in the Colonies.

We must take the liberty of mentioning that, in the title of this treatise, "chemical composition" would be a more appropriate expression than "chemical constitution."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 25, June 20, 1892.

Phenomena of the Residual Life of the Muscle separated from the Living Being. Physiological Action of the Muscular Bases.—Arm. Gautier and L. Landi.—The authors have already shown that the effect of the anaërobic life of the muscular tissue is to acidify and peptonise a small proportion of its proteic substances. A part of the myoalbumen is changed into caseine and into various leucomaines. The fats do not vary appreciably. No glucose can be found in preserved meat, and the glycogen has completely disappeared, being, in the opinion of the authors, partially converted into carbonic acid and alcohol, both of which have been demonstrated. Urea is not produced in any proportion in preserved meat and ammonia, and its salts do not appear in quantities of any importance. Meats if preserved from atmospheric microbia are incapable of undergoing spontaneously the ureic or ammoniacal fermentation. Hence the anaërobic fermentations which occur in muscular tissue free from microbia differ profoundly from the bacterian fermentations essentially hydrating and ammoniacal. The gases emitted by 100 grms. of meat kept for six days at 39° were found to be—

CO ₂	..	..	27.5 c.c.
N	..	..	1.1 "
H	..	..	4.7 "

The easy production of hydrobilirubine in the economy as soon as boron sets in; the reduction of indigo-blue and purple in our organs; the property which muscular flesh possesses of transforming by mere contact and in the cold a small but constant quantity of free sulphur into hydrogen sulphide, shows in what a state of instability is a small portion of the hydrogen which enters into the constitution of the immediate principles of muscle and of its protoplasm. The authors proceed to describe the physiological action of the bases extracted from the muscular tissue.

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By FREDERICK HARRISON, M.A.

Preliminary Examination.

1. HEAT a portion on a porcelain crucible lid; if it chars much and gives off odour of burnt sugar, a tartrate or citrate may be present; if slightly, an oxalate, acetate, or some other organic acid.

2. Add dilute H_2SO_4 , and observe carefully the effect.

Effervescence, without odour ..	= Carbonate.
Warm.	
Red fumes	= Nitrite.
Odour of sulphur dioxide	= Sulphite.
Odour of sulphur dioxide and deposit of sulphur.. .. .	= Thiosulphate.
Odour of sulphuretted hydrogen .	= Sulphide.
Odour of vinegar	= Acetate.
Odour of bitter almonds	= Cyanide.
Odour of bitter almonds and deposit of sulphur.. .. .	= Ferro- or ferri-cyanide.

Add a few drops more H_2SO_4 , and warm with a piece of copper foil.

Red fumes = Nitrate.

Heavy metals, if found, must be boiled out with Na_2CO_3 , filtered, and the filtrate neutralised with dilute HNO_3 .

If the salts are insoluble in water, boil with KHO , filter, and neutralise carefully with dilute HNO_3 .

To a portion of the neutralised cold solution add—

I. $\text{Ca}(\text{NO}_3)_2$ in excess, and filter.

Precipitate (white) = Oxalate, sulphate, tartrate, phosphate, arseniate, borate.

II. Warm filtrate. Precipitate (white) = Citrate.

Filter while hot.

III. To filtrate add $\text{Ba}(\text{NO}_3)_2$ in excess. Filter. Precipitate = Chromate (yellow), sulphate (white).

IV. Filtrate must be divided into four parts.

(1). Add AgNO_3 in excess. All precipitates except curdy white must be disregarded = Cyanide, chloride, bromide, iodide.

(2). Add Fe_2Cl_6 .

Red colour discharged by HCl .. = Acetate.
Blackish = Tannate or gallate.

Blue = Ferrocyanide.

(3). Add FeSO_4 . Dark blue .. = Ferricyanide.

(4). Reserved for proving presence or absence of cyanide by Scheele's test.

Separation of Precipitates I.—Add $\text{HC}_2\text{H}_3\text{O}_2$. Agitate and filter (Filtrate A); insoluble = Oxalate, sulphate. Wash precipitates with a little cold water and percolate with dilute HCl , and neutralise filtrate with NH_4HO ; white precipitate = Oxalate. Percolate any remaining precipitate with boiling water and add to filtrate BaCl_2 ; white precipitate insoluble in HNO_3 = Sulphate.

Neutralise Filtrate A. with NH_4HO ; wash precipitate with cold water, and agitate with cold KHO ; filter and warm filtrate. White precipitate = Tartrate.

Divide any remaining precipitate, after washing, into two parts.

a. Dissolve in HNO_3 , add $(\text{NH}_4)_2\text{MoO}_4$ and warm. Yellow precipitate = Phosphate or arseniate.

To a portion of the original neutral solution add AgNO_3 . Red = Arseniate; Yellow = Phosphate.

b. Dissolve in dilute HCl and moisten a piece of turmeric paper with solution and gently warm. Reddish colour = Borate.

Separation of III.—If yellow, chromate is present. Boil with HCl ; any insoluble white precipitate remaining is Sulphate.

Separation of IV.—(1) precipitated by AgNO_3 . Wash precipitate and percolate with dilute NH_4HO ; neutralise filtrate with HNO_3 . White precipitate = Cyanide or chloride.

If (4) has given reaction of cyanide, boil with HNO_3 . Any insoluble white precipitate is Chloride.

Any white precipitate insoluble in dilute NH_4HO is Bromide or iodide.

Add mucilage of starch and chlorine water. Blue = Iodide; Orange = Bromide.

To prove bromide in presence of iodide, decolourise the blue iodide of starch with excess of chlorine water and agitate with chloroform. Orange = Bromide.

A NEW METHOD FOR THE DETERMINATION OF VANADIC ACID.

By A. ROSENHEIM and C. FREIDHEIM.

THE separation of vanadic acid from those accompanying it in the so-called complex salts is attended with certain difficulties. Thus arsenic and molybdenum, after the reduction of the solution by means of sulphurous acid, have first to be removed by sulphuretted hydrogen, and then for separation from the bases the vanadic acid, after the filtrate has been oxidised with nitric acid, is separated as a mercurous salt. In presence of tungstic acid, the mixed mercury salts of both acids must be dissolved in fuming hydrochloric acid, and after separating the tungstic acid by means of water and precipitating the mercury with sulphuretted hydrogen, the vanadic acid is determined by concentrating the filtrate. Hence, it is often preferred to determine in one part of the substance the sum total of the acids by igniting the mercurous salts with an addition of sodium tungstate, and in another portion to determine the vanadic acid volumetrically, for which two methods come into consideration: the reduction of the compound by means of sulphurous acid in a sulphuric solution and oxidation of the vanadyl formed by potassium permanganate, or distillation of the same with hydrochloric acid with addition of potassium bromide, absorption of the halogen formed in consequence of reduction to vanadyl in potassium iodide, and titration by means of sodium thio-sulphate.

We must, unfortunately, have recourse to such determinations by difference when, e.g., in the compounds containing phosphoric and vanadic acids a direct separation of the vanadic acid in a ponderable form is impracticable, otherwise the application of the permanganate method is limited. In presence of MoO_3 and As_2O_5 (which are also reduced by sulphurous acid) it is entirely excluded, and along with tungstic acid, as formerly shown, the recognition of the end of the titration is rendered very difficult. The method of distillation is more convenient, but, in addition to the variability of the solution of thio-sulphate, it labours under the serious disadvantage that a determination of the alkali appears excluded in consequence of the addition of potassium bromide to the same portion of the substance.

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contain a smaller proportion of water; consequently their valuable constituents are relatively larger in proportion. This point comes into special prominence in the various products used for the food of cattle.

As regards tannin, none of the African woods and barks seem to equal those of Australia, though they exceed those of Europe. The richest, the bark of "beukenhout," contains 15.96 per cent of tannin. By an oversight, the trees are tabulated only by their Caffir or Cape-Dutch names; the botanical names should have been given for identification. Another oversight is that mahogany, acacia, *Abies canadensis*, and *Quercus castanea*, are given as European.

The author's pamphlet is not merely useful in itself, but forms a good example which we hope to see largely followed in the Colonies.

We must take the liberty of mentioning that, in the title of this treatise, "chemical composition" would be a more appropriate expression than "chemical constitution."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 25, June 20, 1892.

Phenomena of the Residual Life of the Muscle separated from the Living Being. Physiological Action of the Muscular Bases.—Arm. Gautier and L. Landi.—The authors have already shown that the effect of the anaërobic life of the muscular tissue is to acidify and peptonise a small proportion of its proteic substances. A part of the myoalbumen is changed into caseine and into various leucomaines. The fats do not vary appreciably. No glucose can be found in preserved meat, and the glycogen has completely disappeared, being, in the opinion of the authors, partially converted into carbonic acid and alcohol, both of which have been demonstrated. Urea is not produced in any proportion in preserved meat and ammonia, and its salts do not appear in quantities of any importance. Meats if preserved from atmospheric microbia are incapable of undergoing spontaneously the ureic or ammoniacal fermentation. Hence the anaërobic fermentations which occur in muscular tissue free from microbia differ profoundly from the bacterian fermentations essentially hydrating and ammoniacal. The gases emitted by 100 grms. of meat kept for six days at 39° were found to be—

CO ₂	..	..	27.5 c.c.
N	..	..	1.1 "
H	..	..	4.7 "

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We must, unfortunately, have recourse to such determinations by difference when, e.g., in the compounds containing phosphoric and vanadic acids a direct separation of the vanadic acid in a ponderable form is impracticable, otherwise the application of the permanganate method is limited. In presence of MoO_3 and As_2O_5 (which are also reduced by sulphurous acid) it is entirely excluded, and along with tungstic acid, as formerly shown, the recognition of the end of the titration is rendered very difficult. The method of distillation is more convenient, but, in addition to the variability of the solution of thiosulphate, it labours under the serious disadvantage that a determination of the alkali appears excluded in consequence of the addition of potassium bromide to the same portion of the substance.

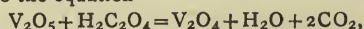
In cases where a gravimetric determination of the

vanadic acid is impracticable, the above disadvantages are avoided by the following indirect method, which dispenses with any titration:—

The vanadic acid or the vanadate, in a sulphuric solution, is reduced to vanadyl by means of oxalic acid, and the carbonic acid evolved is weighed. This method, therefore, approximates to that of Fresenius and Will for the valuation of manganese ore, and that proposed by Vohl for determining chromic acid.

Berzelius mentioned that oxalic acid decomposes vanadic acid, the yellow solution passing through green to blue. But it has nowhere been shown that the reduction in fact goes on to vanadyl. This seems merely to have been inferred from the blue colour of the solution, which is the less permissible as vanadous oxide in a sulphuric solution displays a lavender-blue tone.

In order to decide if the reaction really takes place according to the equation—



a known quantity of pure ammonium vanadate (the proportion of vanadic acid in which was determined by ignition before each experiment) was decomposed by a mixture of equal vols. of solution of oxalic acid, saturated in the cold, and 10 per cent sulphuric acid, at first at a gentle heat, and afterwards at ebullition, and the carbonic acid evolved was evolved in the potash apparatus. As a decomposing apparatus there was used that first described in Rose-Finkener's handbook, recently improved by Finkener, which, though unfortunately too little known, far surpasses all other apparatus. It was also used for the analysis of the remaining compounds.

According to the above equation 182.4 parts by weight of vanadic acid ($\text{V}=51.2$, the mean of Roscoe's values [$\text{O}=16$]) should evolve 88 parts by weight of carbonic acid of $100\text{V}_2\text{O}_5:48.246\text{CO}_2$. A series of experiments showed that this is the case, whence the above equation is correct and the previous assumption is well founded.

I.—Determination of Vanadic Acid in Vanadates.

In alkaline vanadates the water and the acid may be determined in the same portion. The ignited residue is dissolved in water,—if needful with the aid of dilute sulphuric acid, washed into the decomposing apparatus, and the carbonic acid is then liberated by means of oxalic acid.

II.—Vanadic Acid along with Phosphoric Acid.

If prior to the addition of oxalic acid and sulphuric acid dilute phosphoric acid was added to the solution, the result of the experiment was not altered. Hence the method is available for the examination of the vanadium phosphates.

III.—Vanadic Acid and Tungstic Acid.

Dilute oxalic acid acts as little upon a solution of tungstic acid acidified with dilute sulphuric acid, and leaves the colour of the precipitated acid a pure yellow as upon one which has been acidified with phosphoric acid to prevent the precipitation of tungstic acid. The latter precaution was found superfluous, as oxalic acid produces no precipitation in tungstates except in presence of much sulphuric acid. There are formed apparently stable compounds, the examination of which has been undertaken.

IV.—Vanadic Acid and Molybdic Acid.

As explained above, the examination of vanadium molybdates is attended with difficulties, as their titration with permanganate is impossible. Molybdates are not reduced by oxalic acid, whence the determination of vanadic acid on our method is practicable. The Halverscheidt method is here also available.

The method here described has the advantage over the Halverscheidt method, which is of equally general applicability, in as far as it admits of the determination of the base in the same portion.—*Zeit. für Anorganische Chemie*, vol. i., 313.

ON NATURAL PHOSPHATES.*

By J. LAINSON WILLS, F.C.S.

WHEN your President and Treasurer did me the honour to request me to read a paper on "Phosphates" before the Ottawa Field Naturalists' Club, I hesitated in complying.

"Phosphates" in a general way, as we employ the word in this locality, implies the crystallised mineral apatite, so abundant in certain parts of our Laurentian formation. The good work done by the Geological Survey has from time to time, through its officers, kept us well informed of the localities and peculiarities of the occurrence of the Canadian apatite, by valuable contributions from the pens of Sir Wm. Logan, Sterry Hunt, Vennor, Dr. Geo. Dawson, Torrance, Dr. Robert Bell, and others. At the present time, I understand that Mr. Ingall also, who has been in charge of a special study of our Canadian apatite fields, is about to terminate and publish his preliminary report; so with deference to his opportunities and approaching publication, I could not presume to undertake a paper purely on Canadian phosphates or apatites, as was proposed, but thought it might be acceptable to our members here, to give their attention to a more extended and general consideration of natural mineral phosphates, and hence the title of my paper this evening, instead of being "Canadian Apatite," is "Natural Phosphates" in a general way. My present occupation prevents me from giving much time and study to the preparation of this work, but if, by some generalisation of facts, we can awaken a healthy discussion and exchange of ideas, my humble attempt will not have been useless.

Natural phosphates owe their commercial value to the proportion of phosphoric element contained in them, and are employed as raw material for the manufacture of phosphatic fertilisers, being also sometimes applied in the natural and raw state direct to the soil by the farmer. They are also in demand for the manufacture of phosphorus, baking powders, and some other chemical products. By far the greatest demand for them, however, is made by the manure manufacturers for agricultural requirements, and this demand is yearly increasing at a very rapid rate. The occurrence of natural phosphates presents the most varied and interesting modes of formation, as may be surmised by finding their deposits, not only in nearly every geological system, but in many different series of the same system.

Now in beds which may have a fresh-water or marine origin, now appearing as hardened conglomerate or rocks, and sometimes as sand and loose gravel; then again in vein formation or pockets, sometimes amorphous, at other times crystallised.

In the matter of texture, colour, and other physical characters we find the same endless variation.

The origin of the demand for these phosphatised products is comparatively of recent date. It was only in the commencement of the present century that crushed bones were employed as a fertiliser in agriculture, and, strange to say, only then on account of the gelatin or organic matter they might contain.

The following curious statement, which appeared in a scientific journal in the year 1830, *a propos* of the employment of crushed bones in England, exposed the ignorance on the subject at that day, and reads as follows:—"As to earthy matter or phosphate of lime contained in the bones, we may disregard it. It is insoluble and indestructible, and cannot serve as a manure, even in damp soil and in immediate contact with the roots of the plant."

The suggestion of Liebig, to treat the bones with sulphuric acid, opened a new era, to the utilisation of phosphatic materials in agriculture, and the manufacture of artificial manure was soon established.

* A Paper read before the Ottawa Field-Naturalists' Club.

The illustrious Elie de Beaumont thus expressed himself with regard to the commencement of the mining of mineral phosphates:—"Colbert" has said that France would be lost for want of forests, and everyone perceives that without coal his prediction would soon be accomplished. In his day one would have failed to comprehend how a great country might disappear."

Natural Phosphatic Deposits.

These valuable provisions of Nature are the result of various causes and agencies familiar to the geological observer, and their contained phosphoric acid is mostly due to animal life; and when we say "due" to animal life we wish to imply that animal life is the assimilating and concentrative medium of pre-existing phosphoric acid; whether as sea and fresh-water shells, as fish and animal bones, as excreta of birds and saurians, &c., animal organisms have been from the beginning of life, and still are, the silent but mighty laboratory of Nature, never resting to collect and store up the dispersed molecules of phosphoric acid. Among such are the guano beds of recent epochs, coprolite deposits, bone beds, shell beds, &c.

Nature's operations of bringing these materials or their *débris* together to form whole geological areas are equally varied, but the estuaries and depressions of the sea-bottoms of the different and respective geological periods are recognised to have been the receptacles or store-houses of these wonderful supplies. A curious disposition to concretionary action, displayed by nuclei of certain organisms to absorb and accumulate phosphatic matter, with which the ancient seas abounded, is more easily seen in its effects than explained.

Such is the origin of many odd species of nodules, some varieties of which exist in immense quantities.

The abrupt or imperceptible, but never ceasing, operations of geological arrangement follow the aforementioned accumulations, and we then have new forms of mineralised phosphatic matter, giving rise to conglomerates, breccias, phosphatic limestone, shells and marls, sandy and ablation deposits, &c., and most of the known natural deposits of mineralised phosphate display examples of two or more of these products. For instance, the perplexities experienced just now with some of the exploratory workings of the lately-discovered Florida deposits, are chiefly occasioned by the character of these beds containing boulders, and nodules from pea size to masses of several hundred pounds in weight, fish bones, sharks' teeth, and fossil bones,—in fact *débris* from several geological epochs,—each of these materials naturally varying in purity, and therefore also in commercial value, so that the more successful enterprises may be looked for where regular and homogeneous deposits occur, or some cheap and efficient mechanical means are applied for the separation of the marketable products from the less valuable or worthless intermixtures.

The classification of natural phosphates of lime is, as remarked by Dr. Penrose in *Bulletin* No. 46 of the U.S. Geological Survey, "a matter attended with many difficulties, not only on account of the great variety of forms in which phosphate of lime occurs, but also because many varieties blend into one another, thus often rendering it uncertain to which class a special deposit should be referred," and he adopts the following classification, based mainly on the chemical composition of the deposits, and grouped under the headings thus:—

Mineral Phosphates	Apatites	Fluor-apatites
	Phosphorites	Chlor-apatites
Rock phosphates	Amorphous nodules	Loose nodules
		Cemented conglomerates)
	Phosphoric limestone beds	
	Guanos	Soluble guanos
	Bone beds.	Leached guanos

We shall recognise as we proceed with the study of the various phosphatic deposits formed during the different geologic periods, that by far the greater part owe their origin to animal or organic remains, and we shall see that as soon as the organic compounds of a guano, for example, are dissipated and resolved into their elements, we may consider that the residual products, to all intents and purposes, revert to the mineral state, in accordance with the familiar expression "earth to earth."

We pass over, for the present, the guano of various localities, which, however, will be observed to lie mostly within 10 to 20 degrees of the equator.

We should remember, however, that this product has attained its zenith, both as to quality and quantity, and must cede its commercial importance ultimately to the mineral resources of phosphoric acid, which are before us for our more particular consideration.

We shall find the diagram on the wall which shows the approximate geological position or age of the different phosphate deposits, very useful to our present purpose, and we will commence with the more recently formed or mineralised products.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 21).

III.—THE ANALYSIS OF CUPRIC OXIDE.

DEPRIVED of the support of the results from cupric sulphate, Hampe's oxide determinations possess little more weight than those of any other experimenter. It will be remembered that the values of the atomic weight of copper deduced from this source have varied from 63.1 to 63.5. Such a fluctuation alone, without the confirmatory evidence which has just been given, is sufficient to cause the suspicion of an undiscovered error in cupric oxide.

With the hope of detecting the possible error, a number of analyses of the substance were made under varying conditions and with different samples of material. No difficulty was found in obtaining results varying as widely as those cited above. Part of the cause of this variation was traced to differences in the preparation, and part to differences in the temperature and tension of the surrounding air employed in ignition.† Cupric oxide ignited to constant weight at a very dull red heat lost a very perceptible amount of material upon heating to the highest temperatures which hard glass would bear. On the other hand, copper reduced by hydrogen at the lowest possible temperatures is well known to lose in weight on heating to bright redness. Some of Erdmann and Marchand's experiments (*Loc. cit.*, see p. 236, vol. lxxv.) show that the exhaustion of the tube at the time of weighing makes very little if any variation in the weight of the materials; but from others (*J. Prakt. Chem.*, xxvi., 461), as well as from the fiftieth experiment below, it would appear that exhaustion at the time of ignition introduces a somewhat more serious correction. In this last case the apparatus was necessarily rather complicated, to admit of the ignition and weighing of the copper and its oxide in a Sprengel vacuum, but the full description of the contrivance would demand more space than it is worth. In the four preceding experiments Hampe's method was carefully followed.

The mode of preparation of the cupric oxide was essentially that recommended by Hampe, and described in the

* Jean Baptiste Colbert, born 1619, Minister of Finance to Louis XIV.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

† Compare Bailey and Hopkins, *Jour. Chem. Soc. Trans.*, 1890, p. 269; also Schulzenberger, quoted in *Am. Jour. Sci.* [3], xxvi., 65.

Analysis of Cupric Oxide.
(Weights reduced to vacuum standard).

No. of experiment.	CuO dull redness 550° ±. Grms.	CuO 750°? Grms.	Cu found 400° ±. Grms.	Cu found 550° ±. Grms.	Cu found 750°? Grms.	Atomic weight of copper O : Cu = 16 : x.
46.	2·08491	—	—	1·66405	—	63·26
47.	1·11936	1·11851	—	0·89355	—	63·29 to 63·53
48.	1·06300	1·06253	[0·8490]	—	0·84831	63·23 to [63·62]
49.	1·91703	1·91656	—	—	1·5298	63·20 to 63·29
50.	2·62410	Ignited in vacuum	—	2·0956	—	63·44
						63·37

Proc. Amer. Acad. Arts Sci., xxv., p. 199. In some cases the basic nitrate was not washed with water before ignition, and in other cases it was thus washed. In general, none but platinum vessels were used. Various slight unimportant modifications were introduced, which need not find a place here. The essential conditions to be borne in mind are the invariable use of the nitrate as the source of the oxide, and the variable temperatures employed in the ignition.

The average of results so heterogeneous in nature can naturally have no important meaning, but it is interesting to note the approximation to the old value of the atomic weight. The high value given in Experiment 48 is manifestly only a compensation of errors. From Experiments 48 and 49, the only two in which both materials were ignited at a bright red heat, 2·99909 grms. of cupric oxide yielded 2·37811 grms. of metallic copper. Computing from these data the atomic weight of copper, we obtain the value 63·313, which is comparable with the result 63·312 obtained indirectly through the synthesis of the sulphate as well as with the number 63·346 fixed upon by Hampe. The absolute identity of the first two figures must be attributed to chance, since the agreement of the individual results was not perfect.

These results again pointed to the existence of a volatile impurity in cupric oxide, but no proof was afforded that the impurity was wholly driven off at the temperature of fairly bright redness. The determination of this point, as well as of the nature of the occluded material, became a matter of great importance.

Tests for Impurities.

The first hypothesis suggested was the possible imprisonment of a small amount of water (see Müller-Erbach, *Fahresbericht*, 1885, p. 74). To subject this hypothesis to proof, pure cupric oxide might be dried at a red heat, and reduced by means of carbon monoxide, when of course any occluded water would be set free and might be weighed.

The cupric oxide used in the execution of this plan was some of that which remained from the oxygen research. It had been prepared in the usual manner. The carbon monoxide was made from oxalic and sulphuric acids, and after a preliminary purification with caustic potash the gas was collected over water in a glass gas-holder. From this receptacle it was passed through very large amounts of potassic hydroxide, over calcic chloride and red hot platinum sponge, and finally through a flask containing sulphuric acid and two tubes containing phosphorus pentoxide, before being allowed to come in contact with the material to be reduced.

In Experiment 53—which may be taken as a type—15 grms. of the cupric oxide contained in a hard glass tube were dried at a red heat in a stream of pure air for forty-five minutes. A small weighed phosphoric oxide tube was then connected at the exit, and the current of air was continued for over an hour.

	Grms.
Weight of tube before connection	= 55·1920
" " after " " " " "	= 55·1922

The temperature changed from 15·7° to 16·8° between the two weighings, involving a correction of -0·0001 to the latter weight. The tube therefore gained only the tenth of a milligram, showing the cupric oxide to have reached a constant hygroscopic condition.

During the ensuing reduction with carbon monoxide, the drying tube was again connected with the apparatus. Before the last weighing of the tube, all carbon dioxide was expelled by pure air. The tube weighed 55·2177 grms., showing a gain of 0·0255 gm., or 0·017 per cent of the weight of the cupric oxide.

Two similar experiments led to like results.

Reduction of Cupric Oxide by Carbon Monoxide.

No. of experiment.	CuO taken. Grms.	Water formed. Grms.	Volume of carbon monoxide. Litres.	Weight of H ₂ O for 10 grms. CuO. Grms.
51.	6·90	0·0105	—	0·0152
52.	20·00	0·0347	—	0·0173
53.	15·00	0·0255	5·5	0·0170

Nothing in these results proved that the water was not formed from the oxidation of hydrogen or hydrocarbons possibly contained in the carbon monoxide, and indeed further examination showed that it originated from this source. The metallic copper from the last experiment was immediately oxidised by a stream of pure dry air, and once more reduced with carbon monoxide. Four litres of gas required to reduce the partially re-oxidised copper yielded 19·3 m.grms. of water. Since this water could not possibly have come from the oxidised copper, it must have been solely obtained from impurities in the carbon monoxide. The quantity closely agreed with the amount, 18·3 m.grms., which one would have expected to find from the volume of gas used, upon the basis of previous results. Considering the fact that the volumes of gas were not very accurately measured, the difference is not greater than the experimental error. Hence it may be safely concluded that the carbon monoxide contained about four one-hundredths of a per cent of hydrogen by weight, but that the *cupric oxide retained no appreciable amount of water at a red heat.*

Experiments 54 and 55.—The idea that some cupric nitrate might remain undecomposed in cupric oxide is evidently not a new one, for almost every experimenter upon the subject tested for nitric acid in the water formed during the reduction. It seemed possible, however, that the nitric acid might be reduced as well as the cupric oxide, and hence that the test might not be a sufficient criterion. Accordingly, 5 grms. of cupric oxide were dissolved in very pure dilute sulphuric acid, and several successive portions of water were distilled off from the mixture. After evaporation to small bulk in a platinum dish, the distillates were found to be neutral to methyl orange and acid to phenolphthalein. When the amount of standard alkali necessary to neutralise this acidity had been determined, hydrochloric acid was added and the sulphuric acid present was estimated as baric sulphate. Since the weight of baric sulphate (3·7 m.grms.) was nearly equivalent to the amount of alkali used (0·39 c.c. of a decinormal solution), since no nitric acid was found in the filtrate by the most sensitive tests, and since a very perceptible amount of copper was found there, it may be

reasonably concluded that cupric sulphate had been carried over mechanically in fine drops. A second experiment yielded like results. Hence, so far as this test was concerned, *no nitric acid was to be found in cupric oxide.*

Experiment 56.—The tendency of various oxides to hold carbonic acid even at high temperatures is well known. Thudichum (*Chem. Soc. Journ.*, 1876, [2], p. 364) has observed that, in order wholly to free cupric oxide from this impurity, it is necessary to ignite it in a vacuum. In order to test this point so far as it concerns the present investigation, the following experiment was made. After a small amount of nitric acid had been added to 12 grms. of cupric oxide, the substance was gradually brought to redness and maintained at this temperature for ninety minutes. The material was then rapidly transferred to a flask provided with a stoppered funnel and two bent tubes. One of the latter was connected with two test-tubes containing a clear solution of baric hydroxide, and the other permitted a gentle current of air to be blown through the entire apparatus. Before either baric hydroxide or cupric oxide were added, all the tubes and flasks were, of course, freed from carbon dioxide. Finally, dilute boiled hydrochloric acid was run in at the funnel tube, the cupric oxide was dissolved, and the solution was gradually brought to boiling. A slight bluish precipitate of cupric hydroxide appeared after some time in the first test-tube, while the second remained perfectly clear. The excess of baric hydroxide in the first tube was quickly neutralised with weak hydrochloric acid and phenolphthalein, and the precipitate was filtered off and washed. The absence of barium from this precipitate proved the absence of carbon dioxide from the cupric oxide.

In order to test the adequacy of the method, 3.4 m.grms. of sodic carbonate were added to the cupric chloride through the funnel tube. This quantity yielded only one-tenth the amount of carbon dioxide necessary to account for the difference between the atomic weights of copper in question, but it nevertheless produced a heavy white precipitate in both newly filled baric hydroxide tubes. The precipitate when tested showed large quantities of barium; hence the method was quite competent to decide that the absorption of carbonic acid by cupric oxide was not the error for which search was being made.

Experiment 57.—Although it seemed very improbable that cupric oxide could contain even traces of a higher oxide after ignition at a red heat, proof of the point was not at hand. Accordingly, 4 grms. of the substance were boiled with pure hydrochloric acid in an apparatus somewhat resembling the last one, in which all the joints were of sealed or ground glass. The vapours were driven through a reversed air cooler into bulbs containing a strong cooled solution of potassic iodide. The very small amount of iodine set free after some time was determined by means of sodic thiosulphate. This amount corresponded to 0.05 m.grm. of oxygen, but even this was undoubtedly due to copper in uncondensed spray. Eight-tenths of a milligram of potassic dichromate, subsequently added to the cupric chloride, at once set free more than double this amount of halogen in the bulbs. The method was hence shown to be adequate for the purpose. The results prove the absence of an essential amount of any higher oxide or oxidised nitrogen from ordinary cupric oxide.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Lionel Cooper, 173, Marylebone Road, London, N.W.; James Robson, 1, Maxwell Street, Paisley, N.B.; John King Warry, 15, Grafton Street, Mile End, E.

The following were elected Fellows of the Society:—

As Foreign Members:—Emil Fischer, Würzburg; Carl Graebe, Geneva; Adolph Lieben, Vienna; Hugo Schiff, Florence; Th. Schloesing, Paris.

As Ordinary Fellows:—Percy Targett Adams; John W. Alcock, Arthur Edward Barrows, Horatio Ballantyne, Arthur Sanderson Bleckly, Charles Bayliss, Henry Couldery, Thomas Cockerill, Sir John Evans, K.C.B., Herbert Entwistle, John Gibson, Ph.D., John Fenton Newall, Charles James Norris, Henry Ramsden Redman, Ernest Heber Smith, Fred Whiteley, B.A.

Of the following papers, those marked * were read:—

*33. "Contributions to an International System of Nomenclature. The Nomenclature of Cycloids." By HENRY E. ARMSTRONG.

An account was given of the proceedings at the recent Conference on Chemical Nomenclature at Geneva, and attention was directed to the significance of the chief resolutions.

The main recommendation of the Conference may be said to be that *functional* terminations should be given to all names, i.e., terminations indicative of the class to which the compound belongs. This is a principle which is familiar to English chemists through the operation of the rules laid down by the Publication Committee of the Chemical Society for the guidance of Abstractors, and one, therefore, which will readily find favour in this country.

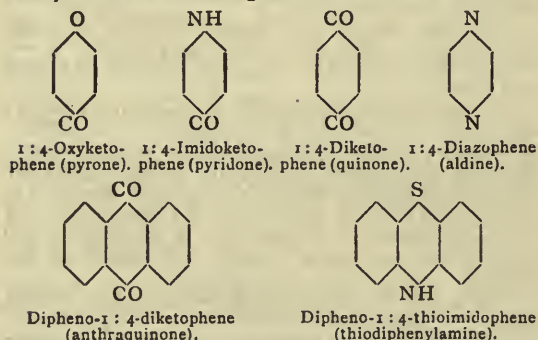
In the case of hydrocarbons, those of the paraffin series, as heretofore, are to receive names ending in *ane*. The termination *ene* is, however, to be restricted to hydrocarbons containing carbon atoms united as in ethylene or ethene, the number of such *ethenoid* unions being indicated by a prefix, e.g., propadiene = $\text{CH}_2:\text{C}:\text{CH}_2$. It is proposed that hydrocarbons containing acetylenic unions should receive names ending in *ine*; this is a somewhat unfortunate recommendation, as this termination *ine* has long been consistently applied to alkaloids by English chemists, and is an illustration of one of the difficulties met with in devising a systematic nomenclature.

Reference was made to the discussion which arose at the Conference on the question whether carboxyl should be treated as a substituting group or no, and to the inconvenience involved in many cases in adopting the recommendation to refer acids to the hydrocarbon from which they might be regarded as derived by oxidation, a proposal which would necessitate that citric acid, for example, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, should be named methylpentanoltitric acid, numbers being added to indicate the position of the OH and CO_2H groups. The motive for this recommendation is doubtless to be found in the desire to maintain a mental picture of a relationship such as exists between alcohol, aldehyd, and acetic acid; but if it be remembered that only primary carbinols are convertible into corresponding aldehyds and acids on oxidation, and that there are no acids corresponding to secondary and tertiary alcohols and phenols, this argument does not appear of great weight. As *ol* is indicative of an OH derivative, there seems no reason why the simple word *acid* should not connote carboxyl, and why *al* should not connote COH; the names ethanol, ethanal, and ethanoic acid, or simply ethane acid, would then stand for the OH, COH, and COOH derivatives of

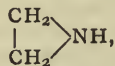
Detection of Turkish Geranium Oil in Oil of Roses.—G. Panajotow (*Ber. Deutsch. Chem. Gesell.*).—Solution of magenta decolourised with sulphurous acid (2 c.c.) mixed with two or three drops of Turkish essence of geranium in the cold gives at first a violet blue colour and after two hours a splendid blue. Oil of roses with the same reagent gives a red colouration only after twenty-four hours.

ethane; citric acid, on this system, would be named propanoltrioic acid or simply propanoltri-acid.

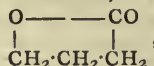
An explanation was then given at some length of the author's proposed system of nomenclature for cycloids, on which he was requested by the Conference to prepare a report. Up to the present time, the termination *ane*, applied to paraffins, has been the only one which has served to connote something more than the possession of a particular function; it has also served to convey definite information regarding the character and constitution of the compound as a whole, as definite in its way as that afforded by the term phenol applied to a particular kind of *ol* or alcohol. It is proposed to apply the term *phene* (perhaps *phen*) to all unsaturated cycloids, and *phane* (perhaps *phan*) to saturated cycloids, the number of terms or members in the cycle to be indicated by the appropriate prefix, although probably in the case of hexaphene (benzene) derivatives it would be unnecessary to use any prefix. For example, names such as furfuran, thiophen, pyrrol, indol are purely empirical and meaningless, in no way serving to indicate the similarity in structure which obtains between the compounds to which they refer, and such names cannot be countenanced much longer; a clear idea of their structure and relationship is at once given, however, by naming such compounds respectively *oxy-* (perhaps *oxo-*), *thio-*, *azo-*, and *phenazopentaphene*. Other examples are the following:—



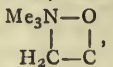
Trimethylene, regarded as a cycloid, might be *triphane*, the name *hexaphane*, or simply *phane*, being assigned to hexamethylene instead of cyclohexane, as proposed by the Conference. The *lactones*, *imines*, *betaines*—in fact, cycloids generally—may be easily named on this same principle, thereby rendering unnecessary a number of specific terminations proposed by the Conference. Thus ethenimine,—



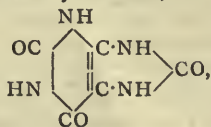
is an *imidotriphane*; the lactone,—



is a 1:2-*oxyketopentaphane*; betaine,—



is *trimethazonoxyketotetraphane*; and uric acid, adopting the formula proposed by Medicus,—



is a *diimidodiketophenodiimidoketopentaphene*.

It is proposed to discuss the subject at length in a comprehensive paper.

DISCUSSION.

Professor Meldola, Mr. Friswell, Mr. Groves, and Mr. Page all spoke in defence of trivial names, and urged the importance of retaining them. Mr. FRISWELL thought the use of *azo* to denote nitrogen in a ring might give rise to confusion, as the term had acquired significance in connection with compounds of a different character. Mr. PAGE dwelt on the importance of giving new names, instead of transferring old ones, to new compounds. Prof. P. F. FRANKLAND thought names unnecessary, and that it would be better for the purposes of a register to use formulæ.

The PRESIDENT said that we must keep in mind that such systematic names as had been suggested were really names of formulæ rather than names of substances. Thus, a name had been suggested for uric acid on the assumption that *Medicus's formula correctly represents the constitution of the acid*. He thought it did, and so do most chemists, but some do not, and for them the name suggested will not be the name of uric acid. Again, a new substance is discovered; its discoverer has no doubt as to its constitution, and gives it the corresponding name—it is written about, is used for preparing other substances, perhaps comes to be made on a large scale, but after a time it is found not to have the constitution indicated by its name: it must then get a new name, and its old name will be given to a substance *now* supposed to have the constitution it indicates. Hence will arise confusion, for when we come across the word in reading we may have some difficulty in ascertaining which substance is meant. Mr. PAGE gave an instance of this kind of confusion—the old hyposulphite had its name correctly enough changed to thiosulphate, but unfortunately the old name, supposed now to be free, was given to Schützenberger's salt. The best way out of this confusion is to abandon the name hyposulphite altogether, and speak of thiosulphates and hydrosulphites. With a rigorously systematic nomenclature we should have no such resource, for the old misapplied name would be wanted for another substance, and confusion would be unavoidable, except by adding in all such cases words sufficient to identify the substance. These words would then be the *name*; the systematic name would be a statement of our opinion as to the constitution. In reference to the objection to the termination *ine* for hydrocarbons with an acetylene union, we could get over this by returning to the old termination *a* or *ia* for bases—morphia, quinia, methyllia, &c. He thought that in translating the French names into English we should as far as possible drop the final *e*, and so bring our pronunciation nearer that of our brethren on the Continent. When the French nomenclature of salts was first introduced into this country, some chemists dropped the final *e* in sulphate, nitrate, &c., and, no doubt, pronouncing these words with the *a* of *hat*, not as we now do with the *a* of *hate*. The confusion would be serious with *ane*, *ene*, *ine*, for an Englishman, unless carefully trained and warned, would be sure to pronounce *ane* almost exactly as a Frenchman pronounces *ène*, and *ene* almost exactly as a Frenchman pronounces *ine*. This would be avoided if we were to spell an, en, in, for, although the pronunciation would not be identical with the French, there would be no risk of mistaking the one for the other, except perhaps in the extremest form of south English, in which an comes so near en as to appear almost identical to those unaccustomed to that dialect.

Mr. GROVES quoted words such as *fat* and *fate* to show that in English we could not dispense with the terminal *e*.

Dr. ARMSTRONG, in reply, said that notwithstanding its disadvantages, a system of nomenclature based on formulæ had become a necessity of the times; trivial names would necessarily still be used, but their use would probably become more and more restricted to substances in daily use. He was satisfied that within a very few years a system of nomenclature would be devised, and, therefore, it was all important that we should contribute our due share to it, and do our best to establish as good a

system as possible adapted for use by English-speaking chemists.

*34. "The Production of Pyridine Derivatives from the Lactone of Triacetic Acid." By N. COLLIE, Ph.D., and W. S. MYERS.

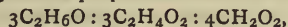
The authors have studied the compound obtained by the interaction of ammonia and triacetic lactone referred to by one of them in a previous communication (C. S. Trans., 1891, 617); they show that most probably it is an α -*di*hydroxy- α -picoline rather than the imidodiketo-compound isomeric therewith. After various attempts to displace the oxygen by chlorine, they at last succeeded in effecting this by means of phosphorus oxychloride; the product possessed all the properties of a dichloropicoline, and when passed together with hydrogen over heated zinc dust gave α -picoline boiling at 128–129°. The melting-points of the platini- and auri-chlorides, and of the picrate prepared from the synthetic alkaloid, were found to be considerably higher than those noticed by former workers, but substances having the same melting-points were ultimately obtained from pure α -picoline, prepared by heating pyridine methiodide. The following are the melting-points observed:—

	B. p.	Platini- chloride. M. p.	Auri- chloride. M. p.	Picrate. M. p.
Picoline from lactone ..	about 128°	216–217° (221–222° corr.)	183–184° (186–187° corr.)	169–171° (172–173° corr.)
Picoline from pyridine ..	127–129°	do.	do.	do.

The platini-chloride prepared from a specimen of bone-oil picoline (b. p. 128–129°), after more than twenty recrystallisations, melted at 210–211°, and the melting-point could not be further raised.

*35. "The Fermentation of Arabinose by *Bacillus Ethaceticus*." By PERCY F. FRANKLAND, F.R.S., and JOHN MACGREGOR.

The products are qualitatively the same as were obtained in the fermentations of glycerol by the same organism, consisting of ethyl alcohol, acetic acid, carbon dioxide, hydrogen, and traces of succinic acid, together with another acid, which was not identified, although its carbon dioxide equivalent was determined. When, however, the fermentation is conducted in a space closed by a mercury seal instead of cotton-wool, a notable proportion of formic acid also occurs amongst the products. The carbonic anhydride and hydrogen are evolved in equimolecular proportions. When the fermentation is conducted in a closed space, the products are formed approximately in the proportions—



the formic acid, as well as the carbon dioxide and hydrogen found, being all collected together as formic acid in this statement.

In the fermentations conducted in flasks plugged only with cotton-wool, on the other hand, the alcohol and acetic acid were in the proportion $2\text{C}_2\text{H}_6\text{O} : 3\text{C}_2\text{H}_4\text{O}_2$. It appears therefore that in the fermentation of arabinose by *Bacillus ethaceticus* the proportion of acetic acid to alcohol is greater than in that of dextrose, and still greater than in that of mannitol and glycerol, but less than in that of glyceric acid.

*36. "Resolution of Lactic Acid into its Optically Active Components." By T. PURDIE, Ph.D., B.Sc., and J. WALLACE WALKER, M.A.

The object of the investigation described in this paper is to show by direct analytical methods that ordinary lactic acid, in accordance with the theory of Van't Hoff and Le Bel, is composed of two oppositely active constituents. Applying the method of Pasteur, which depends on the difference of solubility of the alkaloid salts of active isomeric acids, the authors have resolved ordinary

lactic acid into a dextro- and a lævo-acid by means of the strychnine salt. The strychnine salts of both the active acids are crystallisable, but the strychnine lævo-lactate is considerably less soluble in water than its isomeride. By the fractional crystallisation of the mixed salts and the removal of the strychnine from the crystals and mother-liquors by means of ammonia or barium hydrate, they obtained salt solutions which were respectively dextro- and lævo-gyrate. The dextrogyrate ammonium salt yielded a dextrogyrate zinc salt having the same composition and solubility as zinc sarcocollate. Its specific rotation, +5.63°, indicated, however, that it contained some inactive lactate. A dextrogyrate zinc ammonium salt, $\text{C}_6\text{H}_{10}\text{O}_6\text{Zn} \cdot \text{C}_3\text{H}_5\text{O}_3\text{NH}_4 \cdot 2\text{H}_2\text{O}$, crystallising in well-defined prisms, and having a specific rotation of about +6.49° in an 8½ per cent solution, was also prepared. No corresponding salt of ordinary lactic acid could be obtained. The dextrogyrate salts yielded a lævogyratate acid, which, like sarcocollate acid, yielded an oppositely active anhydride.

The lævogyratate salts obtained from the more soluble strychnine salts were mixed with much inactive lactate, which, however, was mostly eliminated by fractional crystallisation of the zinc salt. Lævogyratate zinc and zinc ammonium salts, similar in composition to the corresponding dextrogyrate salts, were also prepared. The specific rotation of the lævogyratate zinc salt was similar in amount to that of the oppositely active isomeride, that of the zinc ammonium salt being somewhat lower, owing to the presence of inactive salt.

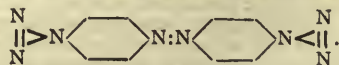
A special experiment proved that the quantities of oppositely active acids separated from each other by means of the strychnine salt possessed equal amounts of optical activity.

When the dextro- and lævogyratate zinc salts with 2 mols. of water were mixed, the less soluble inactive zinc salt was at once precipitated. Fermentation lactic acid is thus shown by analysis to consist of two oppositely active isomeric acids, one of which is identical with dextrogyrate sarcocollate acid, and the other with the lævogyratate acid obtained by Schardinger (C. S. Abstr., lx., 1891, 666) by the bacterial decomposition of cane sugar.

37. "A Method for Determining the Number of NH_2 Groups in certain Organic Bases." By R. MELDOLA, F.R.S., and E. M. HAWKINS.

In the course of an investigation upon which the authors are still engaged, the question has arisen as to whether a certain base contains two NH_2 groups, or one NH_2 and one NH group. The ordinary methods of acetylation, diazotising, the formation of azo-derivatives, &c., having given ambiguous results, the authors have made experiments to ascertain whether in such cases the azoimide could be formed by Griess's method (action of ammonia on the diazoperbromide), as the determination of nitrogen in the pure product would leave no doubt as to the number of NH_2 groups which had been diazotised. As a test case they have started with the symmetrical β -diamido-azobenzene, $(\beta)\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 (\beta)$: this base is not easy to prepare in quantity by the methods usually described, and it was only after many experiments that they found the method patented by the Soc. Anon. des Mat. Color. de St. Denis (Eng. Pat., 1579, January 29, 1890) to be the most direct, although the yield it affords is not very large. According to this method, diazotised paranitraniline is combined with β -naphtholdisulphonic acid in alkaline solution (the G- and R-salts need not be separated), and the purified colouring matter is reduced by boiling with caustic soda and grape sugar. The base thus prepared was purified, diazotised in the presence of chlorhydric acid, and converted into the tetrazoperbromide in the usual way. The latter, which forms an orange crystalline powder, was allowed to remain for some hours in contact with cold dilute ammonia. The product, after several crystallisations from alcohol, forms lustrous silvery scales, melting sharply at 142°. A little above this

temperature it explodes. Analysis confirmed the formula—



Calculated.. .. C, 54.54; H, 3.03; N, 42.42 p. c.
Found C, 54.58; H, 3.33; N, 42.30 ..

The substance is readily soluble in benzene, slightly soluble in petroleum, and crystallises beautifully from hot glacial acetic acid. Nitric acid or sodium nitrite added to the acetic acid solution produces an evanescent magenta-red colouration. The compound is easily reduced both by acid and alkaline reducing agents to paraphenylenediamine; the authors were unable to convert it into a diphenyl base by means of cold stannous chloride.

The method described is recommended for compounds containing NH_2 groups in different nuclei, as the azoimides are well characterised and easily crystallisable compounds. The method which is sometimes adopted, viz., the displacement of the NH_2 groups by a halogen, of course gives the same information, but in many cases this process does not work satisfactorily, and in laboratories where the vacuum method of determining nitrogen is in constant use, the determination of this element is a much simpler operation than the determination of a halogen.

38. "The Existence of Two Acetaldoximes." Second Notice. By WYNDHAM R. DUNSTAN and T. S. DYMOND.

The authors are now able to furnish further information on the change undergone by acetaldoxime when heated (*cf. Chem. Soc. Trans.*, 1892; *Proc.*, 1892, 89). The melting-point of the pure crystals, thoroughly freed from adhering crystals by pressure between blotting-paper, is 46.5° (corr.), the determination being made in a capillary tube. When these crystals are melted and heated at 100° for a few minutes, no apparent chemical change takes place, but the liquid cannot now be crystallised until 13° (corr.). A similar change in the original substance takes place more slowly at 50° , the freezing-point of the liquid gradually falling to the minimum of 13° ; even at 20° this alteration slowly takes place, the crystals gradually melting and furnishing at last a liquid freezing at 13° . At temperatures above 100° the change is very rapid, but unless decomposition occur the freezing point of the resulting liquid never falls below 13° , however long the heating may be continued. This liquid, on exposure at 0° , is very slowly entirely re-converted into the original aldoxime melting at 46.5° .

At first it was thought that the liquid crystallising at 13° entirely consisted of a new modification of acetaldoxime. This, however, is not the case, and so far it has not been possible to crystallise the new modification or even to obtain it in a pure state. The liquid never completely solidifies at 13° . On separating the crystals from the liquid and thoroughly drying them, they melt at 46.5° , and therefore consist of the original substance. The liquid from which these crystals were separated now freezes at a lower temperature than 13° , producing more crystals of the original substance, but on cooling the new residual liquid the freezing-point is found to have risen, and on repeating the operation the freezing-point of the separated liquids rises each time, so that by degrees the whole of the substance is obtained in its original form (m.p. 46.5°).

It is therefore evident that the liquid freezing at 13° is a solution of the original hydroxime in a new liquid modification. This liquid modification cannot be obtained pure, because, on the one hand, there is a limit to the amount of it which can be produced by heating the solid, whilst on the other hand, although a somewhat stronger solution can be made by removing the crystals which separate at 13° , this operation cannot be repeated so as to produce stronger and stronger solutions and finally the pure substance, because at these low temperatures the liquid modification gradually undergoes conversion into the original aldoxime (m.p. 46.5°); and, therefore,

solutions containing less and not more of the new modifications are obtained.

The process by which the new acetaldoxime is formed is therefore a reversible one.

There is only a small difference (0.003) between the relative density of the original substance at its melting-point and that of the solution (l.p. 13°) at the same temperature.

Determinations by Dr. Perkin of the magnetic rotations of the two liquids also exhibit only slight differences; the molecular rotation of the liquid freezing at 46.5° being 3400 and that of the liquid freezing at 13° , 3401.

The molecular weight of the original crystals determined by Raoult's method, using benzene as the solvent, is nearly twice as great as that corresponding with the formula $\text{C}_2\text{H}_5\text{NO}$ (59). The same result was obtained with the solution (l.p. 13°). The two modifications, therefore, have the same molecular weight. When acetic acid is used in the determination of the molecular weight instead of benzene, both the crystals and the solution give numbers closely agreeing with that representing the weight of the gaseous molecule $\text{C}_2\text{H}_5\text{NO}$.

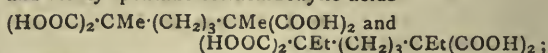
The two modifications of acetaldoxime are therefore isomeric and not polymeric.

When acted on by acetic chloride or anhydride, acetaldoxime is stated to furnish acetonitrile and not an acetyl derivative. In the light of the observations recorded above, it seemed not unlikely that previous observations have been made with a substance consisting largely of β -acetaldoxime. Experiments have therefore been made with α -acetaldoxime (m.p. 46.5°), under such conditions that isomeric change into the β -modification cannot occur during the interaction, as it undoubtedly would if acetic chloride or anhydride were caused to act in the ordinary manner. In this way the authors have obtained what appears to be *acetyl- α -acetaldoxime*. The crystals were gradually dissolved in acetic anhydride, cooled to 0° , and after some hours the liquid was poured into a weak alkaline solution, when an oily liquid separated. This liquid cannot be crystallised, and it does not distil without decomposition. When heated with water it decomposes into acetic acid and acetaldoxime. Solid potash converts it into ammonia and acetic acid. The properties of this compound are being further investigated.

The facts now recorded demonstrate the existence of two isomeric acetaldoximes which seem to correspond in their principal properties with the two benzaldoximes, which, however, are far from stable. The isomerism of the benzaldoximes is now generally adjudged to be stereochemical: although it is probable that this is also true of the acetaldoximes, the authors consider that further experiments are needed before it can confidently be asserted that the isomerism is incapable of a structural explanation. Although it might at first seem that the small difference observed in the magnetic rotations is in harmony with the stereochemical theory, when the magnetic rotations are calculated for the possible structural formulæ, it is found that the differences are also small and are actually too slight to afford trustworthy criteria of structural isomerism.

39. "The Dissociation Constants of Organic Acids." By JAMES WALKER, D.Sc., Ph.D.

The author has determined the dissociation constants of various alkyl derivatives of pimelic acid; of dimethyl- and diethyl-pentane-tetracarboxylic acids—



of several carboxyl derivatives of the polymethylenes; of citric, aconitic, and tricarballic acids; and of a number of acid ethereal salts of dibasic organic acids, $\text{R'OO} \cdot \text{R''} \cdot \text{COOH}$. He finds that the introduction of an alkyl group into the molecule of pimelic acid has little influence on the strength of the acid, which corresponds with Walden's observations on the substituted glutaric

acids. The closing of a carbon chain to form a polymethylene ring is not accompanied by any marked change in the constant. The constants of tricarballic, aconitic, and citric acids, form a series parallel to that formed by the constants of succinic, fumaric, and malic acids, their values being considerably greater, however, corresponding with the greater number of carboxyl groups in the molecule.

Ethyl hydrogen salts of dibasic acids have constants equal in general to about half the constants of the corresponding dihydrogen salts. Exceptions to this rule are only found in the case of dibasic acids with constants abnormally high. Methyl hydrogen salts possess constants somewhat greater than those of the corresponding ethyl hydrogen salts, so that the group COOM has a somewhat more marked acid character than the group COOEt.

40. "Note on the Preparation of Alkyl Iodides." By JAMES WALKER, D.Sc., Ph.D.

The author describes a method for the convenient and rapid preparation of considerable quantities (500–1000 grms.) of methyl or ethyl iodide from iodine, methyl, or ethyl alcohol, and a mixture of red and yellow phosphorus. The apparatus employed is a modification of a fat extraction apparatus, by means of which the iodine is dissolved by the condensed alcohol or iodide, and runs into a vessel containing the phosphorus and alcohol. The method requires little attention, and gives a good yield—570 grms. of ethyl iodide from 500 grms. of iodine. It may also be applied to the preparation of higher iodides.

41. "An Examination of the Products obtained by the Dry Distillation of Bran with Lime." Preliminary Communication. By W. F. LAYCOCK, Ph.D., and F. KLINGEMANN, Ph.D.

Considerable quantities of bran and unslaked lime, in the proportion 1 to 2 by weight, were subjected to dry distillation. The resulting distillate consisted of a black oil floating on an aqueous solution. The aqueous solution smells of herring-brine and contains large quantities of ammonia. On boiling the solution gases are evolved, which burn on ignition with a slightly luminous flame. Amines and furfuran are probably present.

The oil after repeated fractionation was found to have no constant boiling point. Analysis of different fractions showed that they all contained about 4 per cent of nitrogen.

They were treated successively with (1) water, (2) sodium bisulphite solution (the resulting solution contained aldehydes or ketones), and (3) phenylhydrazine. The oils which remained unaffected by this treatment were distilled three times over excess of sodium and eventually fractionated. Analysis showed that the percentage of nitrogen had not been affected to any great extent, but that the substances containing oxygen had been for the greater part destroyed. The percentage of carbon was higher than in the original oil, and, judging from the behaviour of the oil towards agents, indifferent substances, probably hydrocarbons, were present. The oil is evidently a complex mixture, and fractional distillation appears to be of limited use as a means of isolating its constituents.

42. "The Atomic Weight of Palladium." By G. H. BAILEY, D.Sc., Ph.D., and THORNTON LAMB.

The authors have been engaged during the past three years on the investigation of palladium salts and the re-determination of the atomic weight of palladium.

After an examination of the values obtained from various salts, especially potassium palladous chloride (the salt used by Berzelius) and the palladammonium salts, they come to the conclusion that the most reliable substance for the estimation of the atomic weight is palladammonium chloride, $\text{Pd}(\text{NH}_4\text{Cl})_2$. They prepared a series of fractions, and determined the relation between the weight of salt taken and the palladium and chlorine obtained on reducing the compound in hydrogen. The

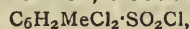
mean of their results from the palladium is 105.46. They point out that the chlorine determinations afford far from accordant values, owing to irregularities arising in the course of the decomposition of the salt and to the difficulty of arresting the whole of the ammonium chloride. The atomic weights of all the platinum metals have now undergone revision, and it is interesting to note that the relations already pointed out by Seubert (*Liebigs Annalen*, cclxi., 279), are even more pronounced when the new value is introduced in place of that obtained by Berzelius (106.35).

Ruthenium.	Rhodium.	Palladium.	Silver.
101.4	102.7	105.5	107.7
Osmium.	Iridium.	Platinum.	Gold.
190.3	192.5	194.3	196.7
Differences ..	88.9	89.8	88.8
			89.0

43. "The Action of Sulphuryl Chloride on Acetorthotoluidide and Acetparatoluidide." By W. P. WYNNE, D.Sc.

1:2:5-metachloracetorthotoluidide is almost the sole product of the interaction of equal weights of sulphuryl chloride and acetorthotoluidide when the latter is suspended in five times its weight of carbon bisulphide. 1:2:5-dichlorotoluene, obtained by hydrolysis of pure potassium 1:2:5-dichlorotoluenesulphonate, boils at 200° under 770 m.m. pressure; on sulphonation with 10 per cent anhydrosulphuric acid at 70–100°, this dichlorotoluene yields a single sulphonic acid, the barium (+H₂O), potassium and sodium (+½H₂O) salts of which are described; the chloride, $\text{C}_6\text{H}_2\text{MeCl}_2\cdot\text{SO}_2\text{Cl}$, crystallises in large tables melting at 43°.

When acetparatoluidide, suspended in carbon bisulphide, is treated with an equal weight of sulphuryl chloride, 1:3:4-metachloracetparatoluidide is the chief product; small quantities of 1:3:4:5-dichloracetparatoluidide and the tri- and tetra-chloro-derivatives being also formed. The corresponding chlorotoluidines are converted into chlorotoluenes by Sandmeyer's method, and these may be separated partly by fractional distillation and partly by fractional sulphonation, since parachlorotoluene is almost exclusively sulphonated by 100 per cent sulphuric acid, 1:3:4-dichlorotoluene by 5 per cent anhydrosulphuric acid, and 1:3:4:5-trichlorotoluene by 10 per cent anhydrosulphuric acid at temperatures below 100°. 1:3:4-Dichlorotoluene, on treatment with 5 per cent anhydrosulphuric acid, yields sulphonic acid, the barium (+2H₂O), potassium and sodium (+H₂O) salts of which are described; the chloride,—



crystallises in long, probably monosymmetric prisms melting at 82°. On hydrolysis of the potassium salt, pure 1:3:4-dichlorotoluene is obtained, boiling at 207° under 764 m.m. pressure. 1:3:4:5-Trichlorotoluene, on treatment with 10 per cent anhydrosulphuric acid, yields a single sulphonic acid, of which the barium (+H₂O), potassium and sodium (+½H₂O) salts are described; the chloride, $\text{C}_6\text{HMeCl}_3\cdot\text{SO}_2\text{Cl}$, crystallises in short, slender needles, melting at 88°. On hydrolysis of the potassium salt, 1:3:4:5-trichlorotoluene is obtained; this melts at 42.5°, boils at 245.5–247° under 768 m.m. pressure, and, on oxidation with dilute nitric acid, yields the corresponding trichlorobenzoic acid melting at 203°.

The action of sulphuryl chloride, therefore, corresponds very closely with that of chlorine on acetortho- and acetpara-toluidide, as described by Lellmann and Klotz (*Annalen*, ccxxxi., 310).

Orthochlorotoluene, on sulphonation with 100 per cent sulphuric acid at 60°, seems to yield only one sulphonic acid, the barium (+2H₂O), potassium (+½H₂O) and sodium (+¼H₂O) salts of which are described; the chloride, $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{SO}_2\text{Cl}$, crystallises in long, flattened, irregularly developed prisms melting at 59°.

Metachlorotoluene, under like conditions, seems to

form only one sulphonic acid, the *barium* ($+H_2O$), *potassium* and *sodium* ($+H_2O$) salts of which are described; the *chloride*, $C_6H_3MeCl \cdot SO_2Cl$, crystallises in brilliant, long, orthorhombic prisms melting at 53° .

Parachlorotoluene is less readily sulphonated by 100 per cent sulphuric acid than its isomerides, and yields two isomeric sulphonic acids, which have not yet been completely separated. Two series of salts are described, one of which is beyond question derived from the mixed acids, as shown by an investigation of the sulphochloride. The results obtained agree in the main with those of Vogt and Henninger (*Ann. Chim. Phys.*, [4], xxvii., 130), and tend to show that the 1:2:4-isomeride, identified by conversion into the 1:2:4-parachlorotolueneortho-sulphonamide described by Heffter (*Annalen*, ccxxi., 209) is the minor product of sulphonation.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, July 4, 1892.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Walter Palmer, B.Sc., and the Hon. Sir Alfred Wills.

The Special Thanks of the Members were returned for the following Donations for carrying on investigations on Liquid Oxygen:—Professor Dewar (Grant from Royal Society), £300; Ludwig Mond, £120; Hugo Müller, £50.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Directory and List of Products of the Chemical Industries of the German Empire. (Adressbuch und Waaren-verzeichniss der Chemischen Industrie des Deutschen Reiches. 8vo., pp. 1164, besides Appendix). Edited by OTTO WENZEL, General Secretary of the Society for the Protection of German Chemical Industries. Third Edition. 1892. Berlin: R. Muckenberger.

THE goodly volume before us may be pronounced at once a movement of persevering industry and of enterprise. No small part of the work, including the title-page, the table of contents, the index of subjects, and the catalogue of chemical products, is drawn up in five languages—German, English, French, Spanish, and Italian. In a large majority of cases the English names of products, &c., are perfectly correct. In a few cases errors have slipped in, such as "sweaty foot" for "sweaty feet." The English chemical nomenclature adopted is not that recognised by the Chemical Society and used in the CHEMICAL NEWS, but an older and less compact system. Thus Herr Wenzel writes "ortho-formiate of ethyl," when we should say "ethyl ortho-formiate." We do not in this country write "jödide," but "iodide."

We notice with pleasure that the author does not indulge in the perplexing medical-pharmaceutical terminology which is little understood outside of Germany, and which causes non-German readers to confound, e.g., chlorates and chlorides, bromates and bromides, &c. Typographical errors are creditably rare in a book written in a variety of languages and dealing chiefly with technical matter.

The work, after the detailed index, gives an index to advertisements, a list of the local associations for protecting the interests of chemical industrialists, a list of the chemical manufactories of Germany, with their trade-

marks, if any, of the analytical, technical, agricultural, and metallurgical laboratories, experimental stations, &c.

Then follows the list of chemicals, with the names and addresses of the manufacturers, the ethereal oils and essences, including compound oils for perfumery (N.B. not "composed oils"), essence not causing turbidity (not "never cloud essences"), manures and cattle-foods, explosives, colours (a most numerous category), fats, oils and lubricants, varnishes, lacquers and polishes (not lakes!). Mattlack had better have been rendered by "dead varnish" than by dull varnish; caoutchouc and gutta-percha wares, resin, pitch and tar, cements, gums and thickeners, coal, charcoal and carbon preparations, mineral waters (here "gicht-wasser" should have been translated not "gouty-water," but "gout-water"), pharmaceutical preparations, photographic requisites, polishing and cleansing materials, soaps, perfumes and cosmetics, waxes and articles of wax, matches, fuses and fireworks.

No one, we think, on carefully reading over this portion of the work before us, can fail to be struck with the enormous magnitude and variety of the German chemical trades and arts, especially if he reflects that the greater part of all this has been the creation of the last half-century. We see here the outcome of that theorising which so many thoughtless persons have derided as useless.

The next portion of the work gives a list of raw materials and of intermediate products, with the addresses of the producers or merchants.

"Blighted corn" is scarcely a good English expression for Mutter korn; it should be "ergotised rye."

Another important section of this Directory includes the agencies, wholesale houses, export and import houses in Germany and other countries.

The towns are given in alphabetical order, and under each the addresses of the houses concerned. Lastly comes the advertisement department.

The entire compilation will be eminently useful to manufacturers and merchants, not merely in Germany, but in all industrial countries.

The entire getting up of the book does very great credit to the publisher, and we hope that the sale will—as it deserves to do—prove amply sufficient to remunerate them for the very heavy outlay which they have evidently incurred.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 2.

Stability of Solutions of Potassium Permanganate.—R. W. Oddy and J. B. Cohen.—From the *Journal of the Society of Chemical Industry*.

Volatility of Sulphuric Acid at Common Temperatures.—G. A. Konfg, also A. Colefax.—From the CHEMICAL NEWS.

Prevention of a Violent Escape of Oxygen.—M. Landolt (*Berg. und Hutten. Zeitung*).—On preparing this gas from a mixture of potassium chlorate and manganese peroxide, the author recommends an addition of potassium chloride, e.g., the residues of a former operation.

Detection of Free Chlorine in Hydrochloric Acid. M. Kupferschläger.—From the *Bull. de la Soc. Chimique*.

Preservation of Sulphuretted Hydrogen-Water.—A. Schneider (*Pharm. Central Halle*).—The author recommends black glass bottles with glass stoppers thickly smeared with vaseline.

Electrolysis.—Thomas Moore.—From the *CHEMICAL NEWS*.—There is added a continuation of the subject by E. F. Smith (*American Chemical Journal*) on the separation and determination of different metals in presence of normal phosphoric acid.

Separation of Ferric Oxide from Alumina.—F. Beilstein and R. Luther.—The process depends on the unequal solubility in water of the basic ferric nitrates and those of aluminium. The precipitated oxides are dissolved in nitric acid, the solution is evaporated on the water-bath, and the residue is allowed to stand on the bath until acid vapours cease to escape. For their detection a test-tube filled with snow or with a freezing mixture is held over the capsule, and the reaction of the water condensed on its sides is examined. The contents of the capsule are covered with hot water, the solid residue is duly crushed up in the water, and—if a small capsule was used—the whole is rinsed into a beaker in which the mixture is boiled for ten minutes. It is then allowed to cool, from 2–3 c.c. of a 10 per cent solution of ammonium sulphate is added, and after depositing the basic iron nitrate is filtered off. As this salt very readily clogs the filter, it is better not to suck the precipitate dry with the water-air pump, but it is collected upon a double filter or filtered through a layer of asbestos placed upon a platinum cone. The precipitate is washed—preferably first by decantation—with a cold dilute solution of ammonium nitrate and finally with a similar hot solution. As it is never practicable to scrape off the precipitate quantitatively from the capsule, the adhering parts are dissolved in dilute hydrochloric acid and reprecipitated with ammonia. The liquid which first passes through often contains a little ferric oxide, although it is perfectly clear and colourless. The detection of iron is easy if we first acidulate the filtrate with hydrochloric acid and then add potassium sulphocyanide. The subsequent portions of the filtrate, however, give no reactions for iron. The first portion of the filtrate (about 100 c.c.) is once more passed through the same filter when it is found perfectly free from iron.

The Electric Conductivity of the Solutions of Organic Acids and of their Salts.—D. Berthelot (*Annales de Chimie et Comptes Rendus*).

Detection of Phloroglucine.—M. Weselsky, further studied by MM. Cazeneuve and Hugounenq.—From the *Bull. Soc. Chimique de Paris*.

Reagent for Hydrocarbons of the Acetyl Series.—A. Béhal (*Bull. Soc. Chimique de Paris*).

The Ultimate Determination of Carbon and Hydrogen.—J. Kjeldahl (*Meddelelser fra Carlsberg Laboratoriet tredje Bind.*).—This paper will be inserted at length.

Solubility of Acid Potassium Tartrate.—Ch. Blarez.—From the *Comptes Rendus*.

Rotatory Power of Camphor dissolved in Oils.—P. Chabot.—From the *Comptes Rendus*.

Quantitative Determination of Phenol.—L. Carré.—From the *Comptes Rendus*.

Determination of Phenols.—J. Messinge and G. Vortmann (*Ber. Deut. Chem. Gesell.*).—The authors propose a volumetric process depending on the formation of iodised phenols. From 2–3 grms. of the phenol are dissolved in soda-lye (free from nitrite), so that to 1 mol. of phenol at least 4 mols. of soda are present. The solution is made up to 250 or 500 c.c., and of this solution 5 or 10 c.c. accurately measured are put in a small flask heated to about 60°, and decinormal solution of iodine is added until the liquid is coloured a deep yellow by excess of iodine, when a precipitate appears on shaking. The liquid when cold is acidified with dilute sulphuric acid, the solution made up from 250–500 c.c., and the excess of iodine is determined in an aliquot part of the filtrate with a solution of sodium thiosulphate standardised to the decinormal solution of iodine. The proportion of

phenol is determined from the proportion given below and the iodine consumed.

Consumption of I.		Colour of precipitate.
1 mol. phenol,	6 atoms I.	 scarlet.
1 " thymol,	4 " "	 brownish red.
1 " β -naphthol,	3 " "	 dirty green.
1 " salicylic acid,	6 " "	 red.

Detection of Pathogenic Bacilli.—K. Ilkewitsch (*München Med. Wochenschrift*).—For detecting the bacilli of tubercle in milk 20 c.c. of the specimen are coagulated with dilute citric acid, the whey is removed, and the caseine inclosing the bacilli is dissolved in a solution of sodium phosphate. The solution thus obtained is well shaken up with 6 c.c. of ether to counteract the action of the fat globules upon the bacilli, the mixture is allowed to stand for the evaporation of the ether, and the mixture is whizzed by means of a modified "laeto-krit" (3600 revolutions per minute). The vessel for the reception of the milk consists of a copper tube, for the bottom of which there is substituted a little basin ground to fit, into which, after the end of the centrifugal process, there is let down a minute copper globe not reaching quite to the bottom (distance 3 m.m.) in order to cover the sediment in the basin. If the centrifugal process does not last longer than fifteen minutes the great majority of the bacilli in the coagulum sink to the bottom of the basin. The copper globe secured to a thread is now let down to the bottom, the supernatant liquid is poured away, the sediment is taken out, distributed into several glasses, stained according to the Ziehl process, and examined with the microscope. With the aid of this method the presence of the bacilli of tubercle were detected with certainty in milk, even when the method of infection gave no results. In examining drinking-water Finkelburg did not succeed in the direct demonstration of Eberth's bacillus in the water by plate cultures, though he succeeded by using the precipitate obtained in the sedimentation apparatus (see *Centralblatt für Allgemeine Gesund.*, x., p. 92).

Detection of Alum in Bread.—M. Schuhmacher-Kopp (*Chemiker Zeitung*).—The author uses the tincture of logwood proposed long ago by Horsley.

Contributions to the Determination of Sugar and Tannin in Wines.—J. H. Vogel.—The author considers it necessary before the determination of sugar, whether in white or red wines, to remove disturbing constituents, especially tannins and colouring-matters.

The Degree of Fineness of Flour.—M. Holz (*Pharm. Central Halle*).—The author uses alcoholic solution of phloroglucine in a 1 per cent solution followed by concentrated hydrochloric acid.

Detection of Sulphuretted Hops.—E. Prior (*Bayr. Brauer-Journal*).—Each experiment is effected as follows:—10 grms. hops are covered in a flask holding 500 c.c. with 200 c.c. of distilled water, which is allowed to remain in contact with the hops for half-an-hour, shaking frequently. The watery infusion is then passed through a folded filter and 50 c.c. of the filtrate are transferred into an Erlenmeyer flask holding 150 c.c. A rod of chemically pure zinc 1 c.m. in length and weighing about 1½ grms. is then introduced, and 25 c.c. of chemically pure hydrochloric acid of specific gravity 1.125. The flask is then closed with a plug of wadding pressed moderately firmly, the lower end of which projecting into the flask has been moistened uniformly with basic-lead acetate.

Examination of the Degree of Oxidation of Linseed Oil Varnish.—W. Fahrion (*Zeit. für Angew. Chemie*).—The author finds his process on the insolubility in petroleum ether of the oxy-fatty acids formed on the oxidation of the non-saturated fatty acids.

The Secondary Alkaloids of Belladonna.—E. Merck (*Merck's Jahresbericht*).—The author shows the

identity of atropamine and apoatropine. An alkaloid obtained by Ladenburg and Roth from Gehe and Co.'s crude belladonnine, and boiling at 242° , as merely pseudo-atropine.

Determination of Total Bases in Cinchona Barks.—W. Haubensaek (*Schweiz. Wochenschrift für Pharm.*).—The author uses known processes.

Detection and Determination of Hydrochloric Acid in the Gastric Juice.—E. Salkowski, M. Rosenheim, M. Hoffmann, and others.—For this paper we must refer to the original, as also for the following papers on the "Quantitative Determination of the Phenols of Human Urine with Bromine" (Th. Rumpf); the "Detection of Hæmatoporphyrine in Urine" (O. Hammarsten); and the "Detection of Peptone" (R. von Jaksch).

Chemico-Legal Detection of Blood.—G. Janecek.—From a special memoir by the author entitled "The Limits of the Demonstrative Power of the Spectrum of Hæmatine and of the Hæmatine Crystals (Teichmann's Crystals) for the Presence of Blood: a Contribution to the Prevention of Judicial Murders." Read before the South-Slavonic Academy of Sciences and Arts, Nov. 7, 1891. Agram: Fr. Suppan, University publisher. The author recommends the spectroscopic investigation for the hæmatine of Stokes, especially since E. Hoffmann has shown its applicability not only to hæmatine but also to oxyhæmoglobine. The object in question is treated with a concentrated solution of potassium cyanide, and the solution thus obtained is examined with the spectroscope. If the cyanide is allowed to act for a sufficient time we see in the spectrum either a distinct broad band in the green, which is very similar to the band of reduced hæmoglobine, or merely a clouding of this part of the spectrum. If we add to the solution a drop or two drops of ammonium sulphide we see the band at once resolved into two bands, which at first sight resemble the bands of oxyhæmoglobine, but may be distinguished by their origin and their position, which is nearer the violet end of the spectrum. Janecek confirms the utility of this method even for the examination of the minutest objects. Thus the blood from bugs and fleas, and also the excrements of these vermin, display not merely the blood spectrum in question but Teichmann's hæmine crystals. The spectrum of hæmatine and of reduced hæmatine can be obtained intensely from the excreta of the house fly, and even hæmine crystals may be easily obtained from even the smallest quantity of fly-dirt; on evaporation the Teichmann crystals may be formed and the absorption spectrum may be obtained.

The Atomic Weight of Rhodium.—K. Seubert and K. Kobbe.—The average result is $R=102.718$, or if reduced for a vacuum $=102.652$.

Determination of the Atomic Weight of Nickel and Cobalt.—Ch. Winkler (*Berichte der Deutsch. Chem. Gesell.*).—The cause of this communication is due to the memoir by G. Krüss and F. W. Schmidt on a "New Element accompanying Nickel and Cobalt."

Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., No. 9.

The Council has adopted a new arrangement concerning "sealed papers." They will be addressed to the President, who will present them at the following meeting, mention of the fact being made in the "Proceedings." The paper will then be delivered to the keeper of the archives, who will give for each a receipt bearing the date of the day when it was received by the President.

On Acid Pyrocatechine Antimonite.—H. Causse.—Already noticed.

Specific Gravity of Textile Fibres.—Leo Vignon.—Already noticed.

On a New Ptomaine.—Dr. A. B. Griffiths.—Already noticed.

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THE CHEMICAL NEWS.

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ON AN OBSTACLE TO SCIENTIFIC PROGRESS.

By Dr. G. GORE, F.R.S.

THE recent recovery of Mr. Waterston's paper from the *Archives* of the Royal Society by Lord Rayleigh, and its publication after having lain there about fifty years (see *CHEM. NEWS*, vol. lv., p. 219), illustrates the less encouragement given in this country to scientific researches containing really original conclusions or phenomena than to any other kinds of such researches.

As scientific researches which are reliable and original are as necessary and valuable as those which consist of accurate measurements without originality, it seems desirable that some arrangement should, if practicable, be made, by means of which such papers as that of Mr. Waterston's (and probably others) would be saved from oblivion, and be, if possible, as competently examined and as fully recognised and published as less original ones. However important a high degree of accuracy of measurement of known phenomena is, the discovery of entirely new phenomena and new truths is essentially more important, for if no new phenomena or truths were discovered, there would be none to be measured. Out of Faraday's simple qualitative discovery of magneto-optic action arose Clerk Maxwell's mathematical theory of light.

A great obstacle, however, to the accomplishment of this very desirable object arises from the following circumstances:—(1) All new truths require to be expressed in new language; (2) In consequence of the fixity of strongly impressed previous ideas in the brain, new discoveries and conclusions are only fully appreciated by a new generation of men; and (3), As the examiners of scientific researches are frequently teachers of long experience, their ideas are apt to become so fixed by long-continued teaching that, notwithstanding their anxiety to do justice to the authors, they are unable to fully understand the new phraseology and phenomena, and therefore discourage the publication of really original researches. The so-called "conspiracy of silence" of scientific men respecting the reality of new scientific discoveries is simply a result of this fixedness of mental impression; the examiners being men of high ability and integrity hesitate to express opinions of matters which they do not fully and clearly comprehend, and other men of science follow their example and remain silent.

It is largely in consequence of this hindrance, and of the almost universal desire of mankind for some *immediate* advantage, that any and every kind of scientific occupation is more encouraged than fundamental original experiment; accounts of inventions and technical investigations are accepted and published as if they were of greater value than the discoveries upon which they are based, and accurate measurements of known phenomena are treated as if they were of more importance than the discovery of new fundamental truths; and the readiness of acceptance and publication of a new truth is often inversely proportionate to its degree of essential importance.

To make laborious and expensive researches, and have them (and especially the valuable experimental evidence contained in them) practically suppressed and consigned to oblivion simply because they are original and cannot be readily understood, is most discouraging and unjust to investigators, a great obstacle to scientific and national progress, and deserves the serious consideration of those publishing bodies who undertake the acceptance or rejection of scientific papers.

Probably the most effectual method of overcoming the difficulty would be for a committee of paid examiners to actually repeat a sufficient number of the experiments, &c., to enable them to arrive at a demonstrable conclusion in each case. This, however, would be an expensive plan, but it would be only a small expense in comparison with that of making the researches themselves, and the importance of the object would justify the cost. The skill and labour required would be too great for unpaid examiners.

The progress of science can never be very satisfactory in this country until this obstacle is removed, nor until scientific men generally treat different problems and truths of science more in accordance with their essential degrees of importance and less according to their extrinsic or *immediate* practical value. Nor will science itself be treated with the highest respect whilst scientific men in general pursue money and trading in knowledge so much more earnestly than knowledge itself. We are all apt to be blinded by the prospect of immediate personal gain, and fail to perceive the deep-seated sources of greater good which lie latent in increased fundamental knowledge. The ideas that immediate personal gain is always the greatest good, and that money is essentially more valuable and a greater source of happiness than knowledge, are only worthy of the darker ages; the greater good, however, takes a longer time to grow. Great good *must* come from new truth, even when we cannot see the way; new facts are the origin of human progress, and great truths are the parents of great uses; there can be no inventions without the facts upon which to base them, and the progress of mankind is greater in proportion as the facts discovered are more comprehensive; for instance, out of the simple qualitative fundamental fact of magneto-electric induction has arisen the dynamo-electric machine and all its world-wide uses. Other similar examples might easily be adduced.

RESEARCH NOTES FROM THE LABORATORY OF MESSRS. CROSS AND BEVAN.

The Production of Acetic Acid from Cellulose and Other Carbohydrates. By J. F. V. ISAAC, B.A. (Oxon.).

ACETIC acid has been frequently identified as a product of resolution by various agencies of the carbohydrates of lower molecular weight, and its relationship to the parent molecule is in many cases easily traced. Cross and Bevan have obtained this acid as a product of the action of sulphuric acid upon the jute fibre (*Chem. Soc. Jour.*, lv., 210), and from cellulose (cotton) by fusion with alkaline hydrates, the percentage yield in the latter case being under certain conditions considerable (*CHEMICAL NEWS*, lxxv., 78). At their suggestion I have undertaken an investigation of this point not merely as empirically of interest, but as affording information of general theoretical value. I take this opportunity of noting the general scheme of the research, with typical results from amongst those already obtained.

"Fusion" of cellulosic substances with alkaline hydrates has been exhaustively studied from the point of view of the production of oxalic acid; and an elaborate paper by W. Thorn (*Dingler's Journ.*, ccx., 25), gives all the necessary data concerning the decomposition of the celluloses in this particular direction.

The production of acetic acid by the method of destructive distillation has also been largely studied, and quite recently by Chorley and Ramsay (*Journ. Soc. Chem. Ind.*, 1892, 395). The important point elucidated by these observers is the occurrence of a specific and exothermic resolution of the compounds of the cellulosic group; of this decomposition, which takes place at about 300°, the acetic acid appears to be a product. It should be noted that Thorn (*loc. cit.*, p. 27), observed the phenomenon also, but under the conditions of fusion with

alkalis, and under this condition at a lower temperature, viz., 180°.

In my investigations the results obtained by the above observers are taken more particularly into account. I confine myself to the decompositions determined by alkaline hydrates at the limits of temperature, 120°—150° and 250°—350°.

As typical members of the cellulose group I have taken cotton cellulose and the "hydracellulose" obtained from the former by the action of hydrochloric acid, and of the lignocelluloses jute and pine-wood. As a compound of more definite constitution to serve as a standard of comparison I have taken cane sugar.

The following factors of the decomposition in addition to temperature as noted above have been investigated:—(1) The nature of the alkali, NaOH, KOH, Ba(OH)₂; (2) Relative masses of carbohydrate and alkali; (3) Additions to the mixture of oxidising agents (e.g., K₂FeCy₆, Fe₂O₃, MnO₂) and reducing agents.

The acetic acid produced has been separated by distillation and determined by titration; checking the results by examining for the presence of other volatile acids and confirming in certain cases by conversion of the acid into silver salt and analysis of the latter.

The numbers obtained for the yields of acetic acid vary from 7 to 40 per cent of the weight of the carbohydrate; the results with the cellulose compounds are similar to those with the cane sugar. There is a considerable production of acetic acid at the lower temperature (125° to 150°), increasing with the duration of the action and also increased, *ceteris paribus*, with the addition of mild oxidising agents: the production of acetic as of oxalic acid is greater with KOH than with NaOH. A considerable production of acetic acid has also been found to occur in certain industrial processes where vegetable fibrous materials are boiled with dilute alkaline solutions (1 to 2 per cent Na₂O) at temperatures not exceeding 110° C.

Under the conditions of my experiments there is, as is well known, a considerable evolution of gas. This will be examined for CO and CH₄ in addition to H.

These researches as far as they have proceeded lead to the following conclusions:—(1) The complex carbohydrates (saccharocolloids) break down ultimately under the action of alkalis at high temperatures similarly to those of lower molecular weight: acetic acid is a main product of the decomposition; (2) The formation of acetic acid at low temperatures indicates the presence of a CO—CH₂ grouping as equally characteristic of the former as of the latter, and from the maximum yields obtained it would appear that it is rather a simple product of resolution than of drastic oxidation, e.g., of alcoholic groups, CHOH and CH₂OH; (3) Observations upon bodies of known composition indicate that this resolution of the celluloses by the alkalis is preceded by the formation of lactic derivatives. The research is in progress, and detailed communications will be submitted in due course.

A Reaction of the Lignocelluloses and the Theory of Dyeing.

The solution obtained by adding potassium ferricyanide to ferric chloride is known to react with many "organic" compounds, prussian blue being formed as the result of the partial de-oxidation of the ferric salt (Watts' "Dictionary of Chemistry," ii., 149). The behaviour of the jute fibre in this solution is remarkable. From dilute solutions the fibre withdraws the ferric ferricyanide, which they may be assumed to contain, exhaustively: increasing in weight in proportion (we have observed a gain in weight as high as 80 per cent), and at the same time converting the compound into a "prussian blue." Analysis of the fibre so dyed show a somewhat variable ratio of Fe:CN, the mean ratio being Fe₄(CN)₁₁. Microscopic analysis shows a homogeneous union of fibre substance and colouring-matter, of which the compound may be said to represent a "solid solution." The reaction does not depend primarily upon a de-oxidation of

the ferric ferricyanide by the fibre substance, for the result is not affected by the presence of other oxidising agents, and both ferric chloride and potassium ferricyanide are only very slowly de-oxidised by the fibre substance in slightly acid or neutral solution. The combination with the ferric ferricyanide we regard as the primary result, and its conversion into prussian blue as the result of a re-distribution of its constituents through the action of the fibre constituent.

The evidence for this view, in addition to the negative points above mentioned, lies in the behaviour of the solution towards other colloids. Gelatin we find gives a greenish coagulum with the ferric ferricyanide, increasing in weight by 20—30 per cent, the reaction being constant as regards increase of weight, and also the quantity of gelatin required to precipitate a given weight of the ferric compound under constant conditions. In this case we have a simple case of interaction between two colloids in solution, the cause lying presumably in the province of solution phenomena, and there is no de-oxidation of the ferric compound.

The phenomena observed in the interaction of the jute fibre substance and that solution we divide, therefore, into the two stages—(1) combination of the two colloids by a species of "coagulation" or mutual "solid solution"; (2) a re-distribution of the constituents of the ferric ferricyanide by a more intimate interaction, within the molecule, with those of the fibre substance.

The latter phenomenon is due to the presence of OH groups of variable functions, which the further investigation of these fibre compounds is bringing more into evidence, such variation as might be inferred from proximity to CO or to CH₂ groups respectively.

In this connection we may cite the results of the researches of L. Vignon on the "Theory of Dyeing" (*Comptes Rendus*, cxii., 623), leading to the conclusion that dyeing depends on the presence of basic and acidic functions in the colouring matter and its absorbent.

We are prosecuting our investigation of these reactions with a view to the further elucidation of the mechanism of dyeing operations, as well as of the constitution of the lignocelluloses.

Determination of Molecular Weights of Cellulose Derivatives (Esters) by the Freezing-Point Method.

Mr. A. Pears, jun., has made a number of observations of the depression of freezing-point of acetic acid determined by solution of compounds of cellulose with acid radicles, e.g., acetates, nitrates, and benzoates. The observations were carried out in a Beckmann apparatus, and with careful attention to the working details prescribed by this observer.

The coefficient of depression was found in all cases unusually high, and was also observed to vary during a succession of observations with the same material.

The solution of these derivatives in acetic acid would appear, therefore, to be attended with dissociation of some kind; we have certainly been forced to the conclusion that the method is inapplicable to these solutions for the purpose of arriving at an approximation to the molecular weights of the derivatives in question.

4, New Court, London, W.C.
July 10, 1892.

ON A NEW BACILLUS FOUND IN RAIN-WATER. By Dr. A. B. GRIFFITHS.

I HAVE detected a new bacillus in rain-water preserved during a mild winter in a barrel exposed to the air (a time when most of the other microbes of water are inactive, and when, consequently, there prevails among them little or no struggle for existence). It is probable that the bacillus of which I am about to speak is derived from the

air, but I have not been able to find it in the atmosphere. The bacteriological examination of the rain-water in which this organism was found gave, in winter, per c.c., 32 bacteria; in spring, 292; in summer, 644; and in autumn, 665.

This species was seen for the first time in 1890, mixed with other microbia developed upon gelatin plates, sown with rain-water diluted with sterilised water; 4 c.c. of this water were diffused in gelatin liquefied at a low temperature and cultivated on plates.

The plate cultures were characteristic. In four days there is formed a small yellow colony, the circumference of which becomes yellowish, turbid, and surrounded with a zone of liquefaction. These colonies vary from 2 m.m. to 1 c.m. in diameter. In a plunge-culture in a gelatin tube the development is no less characteristic. At first from thirty-six to forty-eight hours after inoculation there is formed in the channel of the plunge a slender yellowish band whence there issue in a perpendicular direction numerous straight filaments, especially developed in the upper part, which gives the culture a downy appearance; these filaments increase by degrees, and after four days the gelatin is liquefied progressively. On the surface of the gelatin there appears a brilliant yellow colony.

In broth at 30° this species gives a yellowish scum on the surface, succeeded by a flocculent deposit of the same colour. Upon potato the culture, which grows rapidly, takes an orange colour and slowly converts the starch into glucose. The colouring-matter is insoluble in water, soluble with a yellow colour in alcohol. It dissolves also in benzene, chloroform, ether, and carbon disulphide. It has not been obtained in a sufficient quantity for study. This microbe is a true bacillus; its elements, moderately mobile, vary in length from 2 to 4 μ and in width from 0.6 to 0.8 μ . It does not form spores. It is easily stained with aniline colours, and remains coloured when submitted to the process of Gram or of Weigert. Although discovered in water, this microbe cannot live in distilled water; it requires a certain quantity of organic matter.

The vitality of the cultures resists desiccation, but not heat; a temperature of 100° kills the bacilli in fifteen minutes.

The species does not appear to have any pathogenous action. If pure cultures of this microbe are cultivated for some days upon peptonised gelatin a ptomaine is produced. It is a white solid, crystallising in nacreous needles or in klinorhombic prisms, slightly neutral to test-papers, soluble in 80 parts of water at 17°, very soluble in boiling water, moderately soluble in strong alcohol and chloroform, but not in ether.

The analysis of this formula leads to the formula $C_9H_{21}N_2O_5$. This ptomaine gives a white precipitate with sodium phosphomolybdate, a maroon precipitate with Nessler's reagent, and a yellow with tannic acid. It forms a chloraurate, a chloroplatinate, and a hydrochlorate, all crystalline. It is not appreciably poisonous, but it acts as a powerful diuretic. The author gives this bacillus the name of *B. pluviatilis*.—*Bull. de la Soc. Chim. de Paris*.

ON THE TINCTORIAL PROPERTIES OF AMETHYLCAMPHONITROKETONE AND ITS AUXOCHROMIC GROUPING.

By P. CAZENEUVE.

AMETHYLCAMPHONITROKETONE has a golden yellow colour and possesses tinctorial properties. It dyes wool and silk without mordant in a solution in dilute alcohol. If boiled with common water it decomposes the calcium carbonate of the water, giving a solution of the colour of the alkaline bichromates, and thus dyes wool and silk at the heat of ebullition. In presence of tartaric acid it dyes evenly, but it does not dye in an alkaline bath.

Cotton is not dyed directly, but when once mordanted with tannin it fixes nitroketone.

These facts are interesting in view of the present theories on the fixation of colouring matters upon animal and vegetable fibres. O. R. Witt, in particular, has established a relation between the chemical properties of substances, their colours, and their tinctorial properties. The colourless cyclical hydrocarbons, by fixing certain groups, such as NO_2 , $N=N$, $O-O$, $N-NH$, which the author calls chromophores, become chromogenes; that is to say, substances which are able to form colouring-matters. The subsequent addition of the salifiable groups OH and NH_2 , CO_2H , SO_3H , produces exactly this property of colouring or dyeing, whilst at the same time the colouration of the substance itself becomes more intense. O. N. Witt calls these groups auxochromes.

Amethylcamphonitroketone, which is of a fine golden yellow colour, is a true tinctorial substance; it certainly contains the chromophore NO_2 , but it does not seem to possess the salifiable groups which we have enumerated, and which alone are known hitherto. It departs in several respects from the nitrophenols. Its reactions are readily explained by the presence of an acid CH_2 , by the propinquity of a NO_2 and a CO . We are compelled to admit that this salifiable group, CH_2 , in virtue of its position between NO_2 and CO , gives this ketone its tinctorial properties.

This fact, without being in contradiction with the chemical theory of dyeing, shows at least that the salifiable groups OH and NH_2 , CO_2H , SO_3H are not the only ones which can give colouring properties to a coloured body. Without doubt other instances may be found among the hydrides of the cyclical nuclei.—*Bulletin de la Société Chimique de Paris*.

ON THE INFLUENCE OF THE TEMPERATURE OF COLOURED SOLUTIONS UPON THEIR ABSORPTION-SPECTRA.*

By Dr. H. BREMER.

(Concluded from p. 7).

IN order to heat the solutions to the experimental temperature, 100 c.c. of the liquid were heated as quickly as possible in a flask on the water-bath a little higher than the desired temperature, making up the solvent as it evaporates. The absorption vessel, which has been heated in the meantime, is quickly rinsed out several times with the solution and filled. It is then observed by means of a thermometer warmed almost to the temperature of the liquid until the solution has cooled down to the desired point, which is then at once determined. As colouring-matters are often separated out from their solutions by repeated heating, and as more intense chemical decompositions are often effected, the liquid is always renewed after one determination.

H. Bremer carried out the examination of the coloured solutions in the first place qualitatively, examining the position of the absorptions in the spectrum by means of the universal spectroscope. If a solution has in the absorption-spectrum no bands, but merely one-sided absorptions, the instrument was adjusted with the thread-cross to their margin, and the position of the boundary of the absorption was read off on the drum of the telescope. On adjusting to the limit of absorption the intersection point of the thread-cross was adapted to the point from which no longer a distinct tone of colour was perceptible towards the stronger absorption. Ten adjustments were always made to this point, and their mean was entered in the tables.

* Being Part II. of "Contributions to Quantitative Spectra Analysis," in the *Zeitschrift für Anorganische Chemie*, No. 5.

If bands were present in the absorption-spectrum in question, the maximum darknesses of these bands were aimed at, whilst the solution was gradually diluted in the manner described by G. Krüss (*Zeitsch. Phys. Chem.*, ii., 314). Only in the case of the measurement of well-defined lines the mean of fewer than ten single determinations was taken as the result of observation. For carrying out these qualitative experiments in determining the maximum absorption of the bands, or in ascertaining the boundaries of the absorption, each substance was always examined at the same degree of concentration of its solution, but at different temperatures.

Such qualitative determinations were necessary for properly following up the quantitative determinations of the absorption of light. There appeared in the first place the following results, obtained by examining solutions both of organic and inorganic substances.

On a change of the temperature of a coloured solution there occur in *all cases* displacements of the absorptions in the spectrum. If we wish to determine exactly the position of an absorption band by measuring its maximum darkness, we should always append a mention of the temperature at which the determination was effected. It is most advantageous to work at the mean dwelling-room temperature of 17°·5°, taking care the temperature of the liquid (or of the room) does not vary from this mean by more than a few degrees. In cases of fluctuations of the temperature of the liquid in question of about 6 degrees, qualitative measurements of the absorption-spectra can be effected, the results of which agree sufficiently. It is not admissible to use the solution of a colouring-matter which has had to be dissolved by the aid of heat direct for determination in its hot state without taking its temperature into account.

This dependence of the absorption relations of coloured solutions in the spectrum (certainly determined in all cases) upon temperature must have a distinct influence upon quantitative spectro-analytical determination. Such an influence must make itself felt, because in these determinations we have always, by means of the slit of the eye-piece, to cut out a perfectly definite band of the field of view of the observing telescope (*i.e.*, out of the spectrum), and in this region we must find other conditions of absorption if, owing to a change of temperature of the liquid in question, the absorption is displaced in the spectrum. In this case different parts of the absorption curve of the substance under examination will fall within the limited region at varying temperatures.

The author gives elaborate tables showing the position of the maximum darkness in the spectra of a number of solutions at given temperatures, varying in some cases from 20° to 80°.

Striking examples are contained in the above tables as shown in the determinations for tetraiodfluoresceine potassium and eosine potassium. The maximum darkness of tetraiodfluoresceine potassium dissolved in water lies between the two regions used for quantitative determinations, namely, about λ 525·0, and travels towards the red if the solution is heated. In correspondence the residual strength of light increases on warming in the region λ 501·6 to λ 493·6, whilst in the region on the other side of the band λ 552·6 to λ 540·6, the value of the strength of light falls. In like manner, in eosine potassium the regions λ 508·3 to λ 501·0 and λ 528·3 to λ 521·7, display an antagonistic behaviour, as the maximum darkness of a band lies between both regions at λ 515·9.

Besides, the intensity of the absorption in the spectra of almost all bodies varies on heating. We may measure this by leaving the position of the eye-piece slit in the telescope unaltered, but displacing the telescope so far and in the same direction as the position of the absorption is displaced qualitatively in the spectrum on heating the liquid. As an example for this case we may take the two last measurements of eosine potassium in the regions λ 516·9 to λ 509·8 and λ 518·0 to λ 510·9.

From the above measurements it appears that the tem-

perature of the light-absorbing liquid must be attended to with greater care than heretofore, not only in qualitative but also in quantitative measurements of absorption-spectra. The liquid must not during the observation be heated much more than 5° by radiant heat from the source of light. Otherwise a new specimen of the liquid under examination must be placed in the absorption cell.

If the experimentalist has not the electric light at disposal, and is not willing to introduce between the absorbent vessel and the lamp an isolating stratum for cutting off heat rays, he will do well to select a light which is not too hot, and to make use of the spectrophotometric procedure which gives the highest spectrum, *i.e.*, Vierordt's method.

NOTE ON THE RECENT DISCOVERY OF A NEW SILVER ORE.

By H. N. WARREN, Research Analyst.

THE locality known as Broken Hill in Australia has to all interested in mining operations been recognised from an early period as a vast silver region, and the author has on numerous occasions had attention directed to such minerals as fahlerz, polybasite, horn silver, &c., derived from the above locality, and which from assay of the same have proved themselves valuable metallurgical products. Besides these argentiferous formations there is, however, situated in the same locality immense argillaceous deposits, consisting for the most part of ordinary kaolin.

These deposits have for years been regarded as a waste product on account of the numerous hard particles of horny substance disseminated throughout its structure, thus rendering it unfit for porcelain or other manufacture. The mass of kaolin, as far as can be ascertained, thus remained untouched until the commencement of the present year, when it was again overhauled by some travelling mineralogists, who on applying a few physical tests such as ascertaining the hardness of the particles, &c., at once became struck with their appearance and resemblance to horn silver, and being thus induced to proceed to practical tests, in so doing verifying their supposed theory, the common kaolin deposits at once foreshadow one of the richest silver harvests yet to be gleaned.

I have assayed quite recently a number of samples since the discovery of the same, and find in some the existence of silver iodide only, in others chloride only, whilst in further specimens the existence of both chloride, bromide, and iodide,—the percentage of silver averaging from 7 to 10 per cent, with traces of gold; whilst in other cases samples weighing upwards of 20 lbs. in weight of pure chloride have been obtained.

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THE SEPARATION OF SALICYLIC ACID FROM BENZOIC ACID.

By MISS J. SCHAAP.

THERE does not at present exist a good quantitative process for the separation of these acids, and hoping to effect this I first tried the precipitation with alum. I found, however, that the aluminium benzoate is not quite insoluble in water, so the method is therefore valueless for quantitative purposes. Better results were obtained by the following method.

A few mixtures, each consisting of 0·25 grm. of salicylic and 0·25 grm. of benzoic acid, were dissolved in a sufficiency of hot water and the liquids were then allowed to

cool. The salicylic acid was now precipitated by excess of bromine water, but the question had to be decided whether it was precipitated as the mono-, di-, or tri-bromo compound. I therefore took 0.25 grm. of the bromo-salicylic acid and estimated the bromine by Fresenius's lime method. The nitric acid used was free from chlorine, but the lime was not, so a check had to be made. Allowing for the small quantity of chlorine in the lime, the results in four experiments were, respectively:—0.305, 0.315, 0.319, and 0.314 grm. of AgBr. Theory requires 0.215 grm. for the mono-compound, 0.316 grm. for the di-compound, and 0.374 for the tri-compound; so it follows that the precipitate consisted of the di-compound.

Another question now arose whether the precipitate was sufficiently insoluble in water, and also whether the precipitation was complete. To solve this question 0.25 grm. of salicylic acid was dissolved in water and precipitated with bromine water. Having found that the bromo-compound is very readily soluble in chloroform, I concentrated the filtrate at a temperature of 30° and agitated the liquid with chloroform, which on evaporation did not yield the smallest residue, showing that all the salicylic acid had been precipitated. The precipitated dibromo-salicylic acids were dried in a desiccator and afterwards weighed. The weights were respectively:—0.56, 0.556, 0.551, and 0.553 grm., theory requiring 0.536 grm.

In order to directly estimate the benzoic acid, the filtrates were rendered faintly alkaline with sodium carbonate, and evaporated to a small bulk on the water bath to expel the excess of bromine. The residues were then put into separatory funnels, acidified with hydrochloric acid, and shaken out with chloroform. This was filtered through a dry filter and allowed to spontaneously evaporate in weighed glass dishes. The results were respectively:—0.272, 0.261, 0.237, and 0.232 grm. of benzoic acid instead of 0.250 grm.—*Ned. Tydschr. v. Pharmacie, &c.*, July, 1892.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

By the term "sugar analysis" it is understood that the analysis of all the common saccharine substances, viz., sugar, molasses, syrup, starch, sugar, and honey, are embraced. In the following directions an attempt will be made to indicate the general principles which should guide the practice of sugar analysis, together with sufficient detail to enable these analyses to be carried out with accuracy and uniformity.

The principal components to be determined in the substances mentioned above are:—

- | | |
|------------------------|------------------|
| 1. Water. | 5. Sucrose. |
| 2. Ash. | 6. Lactose. |
| 3. Nitrogenous bodies. | 7. Starch sugar. |
| 4. Reducing sugar. | 8. Raffinose. |

Water.

In Sugar or Melada.—Weigh from 2 to 5 grms. into a flat dish (nickel or platinum) and dry at temperature of boiling water for three hours; cool in desiccator and weigh; return to oven and dry for one hour. If on weighing there is only a slight change of weight, the process may be considered finished; otherwise the drying must be continued until the loss of water in one hour is not greater than 0.20 per cent.

In Honey or Molasses.—(a). Proceed as above, using only 1 to 2 grms. of substance.

(b). Place 2 to 3 grms. of substance in a flat dish holding from 30 to 50 c.c.; dissolve in 70 per cent alcohol, using a small stirring-rod, which is weighed with the dish. Add from weighing bottle 15 to 25 grms. pure dry sand;

dry in oven at 70° to 80° C. until alcohol is nearly driven off; moisten thoroughly with 99 per cent to absolute alcohol; dry at 75° C. for thirty minutes, then at temperature of boiling water for an hour; repeat as above, deduct weight of added sand, and make usual calculations.

Ash.

a. Take 5 to 10 grms. of the material (sugar, molasses, honey) in platinum dish* of 50 to 100 c.c. capacity, heat at 100° C. until water is expelled, and then slowly until intumescence ceases. The dish is then placed in muffle and heated at low redness until a white ash is obtained.

b. *Soluble Ash.*—Digest ash with water, filter on to Gooch crucible, wash with hot water, dry residue at 100° C., and weigh. Difference of weights equals soluble ash.

c. Use 50 m.grms. zinc oxide to 25 grms. molasses or 50 grms. sugar. Incorporate thoroughly by adding dilute alcohol and mixing, dry, and ignite as above. Deduct weight of zinc used from weight of ash.

d. Carbonise the mass at a low heat, dissolve soluble salts with hot water, burn residual mass as above, add the solution of soluble salts, and evaporate to dryness at 100° C.; ignite gently, cool in desiccator, and weigh.

e. Saturate sample with H₂SO₄, dry, ignite gently, then burn in muffle at low redness.

f. Dissolve 10 grms. of sugar in hot water and filter to remove sand, &c.; evaporate filtrate and washings to dryness; carefully carbonise and extract with hot water until there is no longer any reaction for chlorine. Dry and ignite residue; weigh as insoluble ash. Add the soluble portion, treat with HCl in slight excess, and evaporate to dryness. Heat until all free HCl is driven off; take up with H₂O and a little HCl, filter, and wash. The residue is silica. Add NH₄OH, to filtrate, boil and filter, wash residue, which is iron and alumina. To filtrate add (NH₄)₂C₂O₄, evaporate to dryness; ignite and moisten with (NH₄)₂CO₃ and re-ignite; dissolve in water, filter, and wash. Residue equals carbonates of Ca and Mg. Evaporate filtrate to small bulk, add (NH₄)₂CO₃, and evaporate to dryness; drive off excess of ammonia cautiously and weigh. This gives the alkalies as carbonates, and this weight added to the insoluble ash, formerly determined, gives the total carbonate ash.

Nitrogenous Bodies.

Any of the methods adopted by the Association for the estimation of nitrogen may be used.

Reducing Sugar.

Reagent, Alkaline Copper Solution. (Fehling, Violette).

- 34.64 grms. pure crystallised copper sulphate.
187.00 grms. tartrate soda and potash.
78.00 grms. caustic soda.

Dissolve the CuSO₄ + 5H₂O and make up to 1000 c.c. at the average temperature at which the analyses are made. Mix the solutions of Rochelle salts and caustic soda and make up to 1000 c.c. In practice use equal volumes of each reagent.

Processes (Volumetric).—a. The solution to be examined should contain about 1 per cent of reducing sugar. To 10 c.c. of the copper solution and 10 c.c. of the alkali, in a large test tube, add 20 c.c. of water, and boil. Add the sugar solution in approximately the proper quantity to reduce the copper, and boil for exactly two minutes. If, on standing for a moment, the solution is, still blue, add more sugar solution and re-boil. When no longer able to distinguish any residual copper by the eye, suck a few drops of the boiling hot liquid into an end reaction tube and test the filtrate for Cu with ferrocyanide of potassium solution and acetic acid. If copper be still present, add the sugar solution little by little, boil, and re-test until no copper is found. Having thus determined the approxi-

* If the substance contains tin or other metal capable of uniting with platinum a dish made of some other material must be used.

mate quantity of sugar solution to be used, repeat the test twice, adding at first each time almost the entire quantity of sugar solution necessary to complete reduction.

b. Gravimetric.—Take 25 c.c. of copper solution of following composition:—

34·639 grms. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ in 500 c.c. of water, add in Erlenmeyer flask 25 c.c. of alkali solution made as follows:—

173 grms. Rochelle salts }
51·6 grms. NaOH } in 500 c.c. water.

Add 50 c.c. of a sugar solution of such strength as to leave a part of the copper unreduced; heat quickly to boiling point and boil for exactly two minutes; add 100 c.c. recently boiled cold distilled water. The liquid is poured at once into a filter tube made of hard glass with asbestos diaphragm (an ordinary extraction tube is well adapted for this purpose). The asbestos film should be previously moistened. Bring finally all the separated suboxide into the tube with the help of a feather brush, and wash with 300 to 400 c.c. of boiling water; afterward with 20 c.c. absolute alcohol, and finally with ether; then dry, heat to low redness to convert into oxide and to destroy any organic matter. The copper may also be weighed in the metallic state after reduction in a stream of dry hydrogen. The tube should in all cases be kept in a desiccator before weighing.

c. Gravimetric.—Reagents:—

34·639 grms. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ }
125·000 grms. NaOH } in 500 c.c.
173·000 grms. Rochelle salts }

Process.—In a beaker of 250 c.c. capacity place 25 c.c. each of the reagents and 50 c.c. of water. Heat to boiling and add 25 c.c. of the solution to be tested, which should contain about 1 per cent of reducing sugar (dextrose, levulose). Boil for exactly two minutes, decant into a Gooch crucible, wash by decantation with 100 c.c. of boiling hot water, keeping the cuprous oxide in the beaker constantly covered. Place the beaker containing the cuprous oxide in place of the one receiving the wash water and dissolve the Cu_2O in a Gooch crucible in a fine stream of HNO_3 ; wash until all $\text{Cu}(\text{NO}_3)_2$ is removed. Transfer the whole of the nitrate from the beaker to a tared platinum dish, add a little H_2SO_4 , and evaporate over steam bath until all HNO_3 is expelled and the Cu is converted into CuSO_4 ; connect with battery of four gravity cells and allow electrolytic action to continue for three hours or until all the Cu is deposited. (Connect the dish with the zinc pole of the battery). Pour off the acid solution, adding water until all trace of H_2SO_4 is removed; wash with 95 per cent alcohol and finally with absolute alcohol; ignite residual alcohol, cool in desiccator, and weigh; calculate sugar reduced from weight of metallic copper by the following factors:—

1. Multiply weight of copper by 0·5698 for weight of invert sugar.

2. Multiply weight of copper by 0·5808 for weight of anhydrous dextrose.

These factors are correct only for a copper solution of above strength and reducing sugar of approximately 1 per cent strength.

Sucrose.—(Optical method, to be used when the sugar is approximately pure).

a. Dissolve 26·048 (for the Ventzke), (16·19 for the Laurent scale) grms. of sugar in water at temperature at which the polarisation is to be made, and, after clarification, make the volume up to 100 c.c. The sugar is conveniently weighed in a counterpoised nickel or German silver dish with large lip, whence it is readily washed into the flask. The solution before being filled to the mark is clarified by the addition of lead subacetate or phosphotungstic acid until no further precipitation takes place. Excess of lead should be avoided. The filtration and clarification may often be helped by adding a few drops of suspended aluminic hydrate after the lead.

The flask is filled with pure water until the lower line

of the meniscus coincides with the mark on the neck. The mouth of the flask is closed with the thumb and its contents well shaken, and poured into a folded filter; the first 15 to 20 c.c. of the filtrate are rejected. The subsequent filtrate, if not perfectly clear, is returned to the filter, and this continued until the filtrate shows no cloudiness. A 200 (100 to 500) m.m. tube is filled with the solution, placed in the polariscope, the scale of which, after neutralising the rotation produced by the sugar by turning the analytical prism or moving the quartz wedge, will give the percentage of sucrose in the sample taken. A dark solution may either be read in a 100 m.m. tube or the solution may be decolourised by shaking it with a small quantity of dry bone-black. A weak solution may be read in a tube from 300 to 500 m.m. in length.

b. Optical Method by Inversion.—For raw sugars, molasses, &c.

1. *Method of Clerget.*—Make up the solution as above and place 50 c.c. of the filtrate in a flask marked at 50 and 55 c.c. Fill to upper mark with strong HCl and mix well; place in hot water and heat quickly to 68° C.; keep at this temperature for exactly ten minutes; remove, cool quickly to room temperature, and polarise, noting temperature. If the sample contained originally any invert sugar the second polarisation should be made at approximately the same temperature as the first. The percentage of sucrose is then calculated by the following formula:—

S = percentage of sucrose.

a = first polarisation.

b = second polarisation (usually to the left).

$a + b$ = sum of the polarisations.

t = temperature of observation in degrees C.

Then—

$$S = \frac{a + b}{144 - \frac{t}{2}}$$

When b is to the left, a and b are to be added; when b is to the right, it is to be subtracted from a .

2. *Method of Lindet.*—Place 50 c.c. of the filtrate as above in a flask marked at 100·5 c.c., add 5 grms. of powdered zinc (zinc dust), place in boiling water, and when at boiling point add, little by little, 5 c.c. of strongest HCl. After the acid has all been added, cool and make up to mark. Polarise in a 400 m.m. tube, or multiply the reading in a 200 m.m. tube by 2. Calculate percentage of sucrose as before.

Gravimetric Method.—Determine first any reducing sugar in sample by methods mentioned above; then invert sucrose, neutralise free acid, and re-determine the reducing sugar. Deduct the percentage of reducing sugar obtained at first, and the remainder will be reducing sugar derived from sucrose; multiply this number by 95 to obtain percentage of sucrose in sample.

Lactose (Anhydrous).

Take 20·56 grms. (16·19 sucrose) or 32·99 grms. (26·048 sucrose) dissolve, clarify if necessary, and complete volume to 100 c.c. The reading of the vernier scale of the instrument will give the true percentage of lactose. The lactose may also be determined by the alkaline copper method, 10 c.c. standard Fehling solution is equal to 0·067 grms. lactose. The weight of copper reduced multiplied by 0·7635 = lactose.

Lactose in Milk.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:—

Reagents.—1. *Basic plumbic acetate*, specific gravity 1·97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One c.c. of this will precipitate the albumens in 50 to 60 c.c. of milk.

2. *Acid mercuric nitrate.* Dissolve mercury in double

its weight of nitric acid, specific gravity 1.42. Add to the solution an equal volume of water. One c.c. of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric iodide with acetic acid.* KI, 33.2 grms; HgCl₂, 13.5 grms.; C₂H₄O₂, 20 c.c.; H₂O, 64 c.c.

Apparatus.—1. Pipettes marked at 59.5, 60, 60.5 c.c. 2. Sugar flasks marked at 102.4 c.c. 3. Filters, observation tubes, and polariscope. 4. Specific gravity spindle and cylinder. 5. Thermometers.

Manipulation.—1. The room and milk should be kept at a constant temperature. It is not important that the temperature should be of any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the result for analytical purposes. The temperature selected should be the one which is most easily kept constant.

2. The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required, use specific gravity flask.

3. If the specific gravity be 1.026, or nearly so, measure out 60.5 c.c. into the sugar flask. Add 1 c.c. of mercuric nitrate solution, or 30 c.c. mercuric iodide solution, and fill to 102.4 c.c. mark. The precipitated albumen occupies a volume of about 2.44 c.c. Hence the milk solution is really 100 c.c. If the specific gravity is 1.030, use 60 c.c. of milk; if specific gravity is 1.034, use 59.5 c.c. of milk.

4. Fill up to mark in 102.4 c.c. flask, shake well, filter, and polarise.

NOTES.—In the above method of analysis the specific rotatory power of milk sugar is taken at 52.5, and the weight of it in 100 c.c. solution to read 100° in the cane-sugar scale at 20.51 grms. This is for instruments requiring 16.19 grms. sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk sugar, whatever instrument is employed.

Since the quantity of milk taken is three times 20.51 grms., the polariscopic readings divided by 3 give at once the percentage of milk sugar when a 200 m.m. tube is used.

If a 400 m.m. tube is employed, divide reading by 6; if a 500 m.m. tube is used, divide by 7.5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102.4 for 60 c.c. no correction for volume of precipitated casein need be made. In no case is it necessary to heat the sample before polarising.

(To be continued.)

ON NATURAL PHOSPHATES.*

By J. LAINSON WILLS, F.C.S.

(Continued from p. 29).

OCCURRENCE OF NATURAL PHOSPHATES IN THE GEOLOGICAL EPOCHS.

Post-tertiary or Quaternary System.

True guanos.

Crust or "leached" guanos.

West Indian and Pacific phosphates.

Tertiary System.

West Indian rock phosphates.

Nassau or Lahn nodular concretions.

Suffolk coprolites in the Red Crag and Coralline Crag. (Reposing on the Lower Eocene.)

S. Carolina beds, resting upon Eocene.

* A Paper read before the Ottawa Field-Naturalists' Club.

Deposition of Florida phosphate *débris* and organic remains.

N. Carolina overlying Eocene marl.

Fundamental rock of Florida phosphate deposits.

Clays and *débris* of Bordeaux phosphates.

Cretaceous System.

Belgian (Liege) Hesbaye nodules.

American Alabama amorphous nodules.

New Jersey marls.

Belgian (Mons) Ciply nodules (Maestricht beds).

Somme deposits, arenaceous and nodules.

Russian "Samorod" nodules Desna-Don.

Cambridgeshire and Bedfordshire coprolites.

French nodules of Ardennes, Meuse.

" " Montpellier and Bellegarde.

Oolitic or Jurassic System.

Bordeaux phosphorites and nodules overlain by tertiary (eocene) clays and *débris*.

Algerian phosphates.

Triassic System.

Highly phosphatic beds (between trias and below lias) containing exuviae of huge reptiles as well as remains of fish and crustaceans.

Permian System.

(Appearance of reptilia).

Carboniferous System.

(Appearance of amphibia).

Devonian or Old Red Sandstone.

Highly phosphatic beds in conjunction with lower carboniferous.

Highly phosphatised beds in Shropshire containing oldest known remains of vertebrate life associated with crustaceans.

Silurian System.

(Appearance of vertebrata).

Welsh Bala beds. Berwyn phosphate mine.

Lingula flags (Quebec) 40 per cent tribasic.

Angers slates (France).

Phosphate limestone of Kentucky.

Logrosan (Spain) phosphorites (apatites?).

Caceres (Spain) "

Portugal phosphorites.

Cambrian System.

(Appearance of protozoa, mollusca, annuloida, and crustacea).

Laurentian System.

Canadian apatite.

Norwegian apatite.

Thus at the present time we have mineral phosphates of lime in process of formation, and principally known in commerce as "crust guano."

Looking at the chemical composition of average bird guano, we find it to be composed of the following constituents:—

Moisture..	15.8
Organic matter and ammoniacal salts	52.5
Phosphates of lime	19.5
Phosphates of iron and alumina	3.1
Alkaline salts..	7.6
Silica and sand	1.5

This typical analysis is from the average of fifteen samples made by Nesbit on the Chinchas Inland guano.

An elementary knowledge of chemistry will assist us to perceive what a large proportion of the above constituents will be leached out by water or dissipated by prolonged exposure to ordinary atmospheric influences,

especially when we remember that the organic matter above mentioned comprises uric, oxalic, and phosphoric salts of alkalis and ammonia, and even about one-third of the phosphates of lime is found to be soluble in water. Given a deposit of guano on a limestone soil or rock, and it is readily perceived that every shower will contribute to the steady but continual process of the transmutation of the carbonate of lime into phosphate of lime in consequence of the discharge of the weaker carbonic acid by the stronger phosphoric acid.

The exhausted guano then becomes phosphatic in distinction to being nitrogenous and ammoniacal ("leached"), and the subjacent limestone undergoes a metamorphosis by a double decomposition into phosphate of lime. If the absorbing limestone is pure, the phosphate of lime formed thereby will be correspondingly pure; and on the other hand, if the calcareous base is intermixed with clay or sand or ferruginous material, the newly formed product will contain alumina, silica, oxide of iron, &c., in like proportions.

Such has been the undoubted origin of the deposits of Aruba rock phosphate, samples of which are on the table, and which are typical of this kind of metamorphosis and will serve to illustrate many similarly formed deposits, notably those of Curacao, Sombrero, Navassa, and Redonda (in which latter case the subsoil must have been aluminous, since the mineral is a phosphate of alumina).

In some cases the phosphatic principle may have been derived from animal *debris*, such as bones.

The composition of animal bones varies somewhat according to the animal furnishing them, and even with the particular part of the same animal; but the following analysis, expressed in 100 parts, may be taken as an average:—

	Green bones.	Bone ash.
Moisture.. .. .	33.0 (gelatin)	
Organic matter .. .	56	70—75 per cent.
Phosphate of lime . . .	3	
Phosphate of magnesia . .	3	
Carbonate of calcium . .	4	
Alkaline salts		
Silica		

The bones of birds are even richer in phosphoric acid than those of animals, but bones of amphibia and fish contain less than those of birds and animals.

Amongst other animal organisms rich in phosphoric acid or phosphate of lime may be mentioned certain shell fish, or rather their shell remains, notably the shells of *Lingula* and *Orbicula*, which consist for the greater part of phosphate of lime, and are found in accumulated beds in the Lower Silurian rocks, being thus described by Sir Wm. Logan ("Geology of Canada," 1863).

Those coming from the Chazy formation at Alumette Island left after calcination 61 per cent of fixed residue consisting of—

Phosphate of lime	85.7
Carbonate of lime	11.7
Magnesia	2.6

100.0

and analysis of the original material gave as follows:—

	Alumette.	Hawkesbury.	R. Ouelle.
Phosphate of lime	36.38	44.70	40.34
Carbonate of lime and some fluorine	5.00	6.60	5.14
Carbonate of magnesia .. .	—	4.76	9.70
Oxide of iron and alumina ..	7.02	8.60	12.62
Magnesia	—	—	—
Insoluble	49.90	27.90	25.44
Volatile by heat	1.70	5.00	2.13
	100.00	97.56	95.37

We here observe an average of 40 per cent of phosphate of lime. It would appear that our knowledge of the pro-

portion of phosphatic element in similar animal remains is very imperfect, so that upon further investigations we may expect to meet with many other similar accumulated supplies of phosphoric acid.

Some authorities attribute a large portion of the phosphate of lime in the Charleston fields to such molluscs and principally *Lingula pyramidata*, which are found abundantly on the present coast.

Classification of Natural Phosphates.

I prefer for all practical purposes and from rational observation to modify the classification proposed by Dr. Penrose, thus:—

Apatites	{ Fluor-apatites. Chlor-apatites.
Mineral and rock phosphates	{ Phosphorites. Nodules, coprolites. Concretions. Conglomerates. Phosphatic limestone. Phosphatic marls. Crust guanos.
Guanos	{ Nitrogenous. Phosphatic, or leached. Bat guano.
Animal remains	{ Bone beds. Shell beds. Animal exuviae.

We will now proceed to trace in a cursory way the commercially known deposits, commencing with the most recent and passing stratigraphically in descending order to the more ancient formations.

Guanos.

Guanos are of two kinds,—nitrogenous or those containing their original manurial qualities, and phosphatic or "leached," the latter being in a more or less mineralised condition by exposure to weathering.

Among the nitrogenous guanos we have the Peruvian, Ichaboe, Patagonian, and Falkland Islands.

The phosphatic or weathered guanos include those of the Pacific or Polynesian Islands, Sydney, Phoenix, Starbruck, Baker, Howland, Jarvis, Enderbury, Malden, Lacedpede, and Arbrohlos Islands.

Some of these deposits are more or less exhausted, and new islands furnishing similar products are from time to time worked.

The West Indian guanos are from Aves, Mona, Tortola.

Other South American are Patos Islands, Megillones, Rata.

From Africa, Saldanta Bay and Kuria Muria Islands.

Bat guano, the product from the floors of caverns inhabited by bats, have sometimes been sent to market as a rich fertiliser. It is found notably in Cuba (W. I.) and in N. Borneo. It possesses a characteristic dark brown colour, and exhibits the undigested parts of beetles' wings and insect *debris*.

Bone Beds.

These are found in nearly all sedimentary strata from the Devonian up to the present time, but with the appearance of those remarkable reptilia in the Permian age we find that these kinds of phosphatic provisions of nature took enormous developments, augmenting the resources previously furnished by the amphibia of the carboniferous epoch.

Bone beds, however, in their original state have furnished little to commercial supplies of phosphatic products, except those found in the tertiary and quaternary ages, such as Bordeaux, Carolina, Florida, and Sombrero (breccia).

Shell Beds.

Since these must have existed from a time well into the paleozoic periods, or that is to say from the Cambrian

age, we may expect and do find these mollusca remains through a wide range of systems and strata and up to recent times.

The Silurian *Lingula* beds are remarkable, and have been already particularised as a probable abundant source of phosphoric acid.

The Welsh Silurian beds and the French Bellegarde and Ardennes deposits in the lower Green-sand (cretaceous) exhibit evidence of this origin, while the tertiary and quaternary phosphates contain very frequently these marine and fluviatile remains as a contribution to their value in phosphate of lime.

Some very interesting specimens are on the table from the Dutch West Indies containing from 75 to 80 per cent of tribasic phosphate of lime, and exhibiting in some cases one mass of shells belonging to recent times.

Coprolites

Owe their name to Professor Henslow, and should be applied only to the fossil exuviae of animals. The appellation has extended itself to many rolled or gravelly products, chiefly found in the cretaceous formation. In England they have been worked to a large extent in Bedfordshire and Cambridgeshire, where they appear in the (Neocomian) strata, between the chalk and the subjacent Jurassic system, in nodules and pebbles of size from a pea to a hen's egg, and sometimes cemented by ferruginous sand into a hard conglomerate; organic remains are present, and casts and fragments of fossils with abundance of ammonites, vegetable remains, and other debris of the Jurassic epoch (*Iguanodon* and *Megalosaurus*, &c.).

The commercial products contain from 45 to 55 per cent phosphate of lime.

The coprolites of Suffolk occur in the tertiary, being in the older pliocene (the red crag and coralline crag). They are poorer in phosphate of lime, more ferruginous and harder in texture.

France also possesses some deposits of this character at Bellegarde, near the Swiss frontier, and also at Montpellier and Avignon, yielding 54 per cent tribasic phosphate of lime.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 31).

The Determination of Occluded Gases.

AFTER so much negative evidence, the only remaining hypothesis which could account for the irregularity of the atomic weight of copper deduced from cupric oxide is that of the occlusion of gases by the substance. This idea is by no means new. As long ago as 1842 Erdmann and Marchand (*Journ. fur Prakt. Chemie*, xxvi., 461), showed that at least a small amount of air was condensed by the substance. Frankland and Armstrong (*Chem. Soc. Journ.*, xxi., 89, 93), found in 1868 that cupric oxide prepared from the nitrate contains both carbonic acid and nitrogen. Hilditch (*CHEMICAL NEWS*, xlix., 37, 1884), states that oxygen gas is occluded by cupric oxide at a red heat, and estimates the effect of this impurity upon the atomic weight of oxygen without, however, adducing any experimental data. More recently Morley (*Amer. Journ. Sci.*, xli., 231, March, 1891), has found that cupric oxide slowly gives off a gas in vacuum. It is a noticeable fact that cupric oxide is almost as serviceable as platinum in preventing bumping during ebullition.

The simplest and surest method for the liberation of an occluded gas is completely to dissolve the cupric oxide in a pure acid. It is by no means certain that indefinite heating in a vacuum would accomplish the end in view. Several pieces of apparatus more or less suitable for the present purpose were devised in succession, and by their means it was proved that some varieties of cupric oxide occlude important quantities of aeriform material. Nearly fifty determinations were made.

According to the first method a tube of the shape shown in Fig. 1 was filled at the end with freshly ignited



FIG. 1.

cupric oxide, and in the middle with pure boiled sulphuric acid. When the whole had been completely exhausted by means of a Sprengel pump, the liquid was allowed to come in contact with the solid, and the gas evidently set free was pumped out and measured. But the action was of course only a very superficial one, and no amount of long standing or violent shaking could accomplish a more complete change. Three experiments indicated that at least a small amount of gas, which appeared to be chiefly nitrogen, was set free. Since it was difficult to decide how much cupric oxide had been combined, the method was abandoned.

Subsequently, more dilute boiled sulphuric acid was used; and the apparatus was sealed by fusion after exhausting, but before mixing the acid and base. The mixture was digested upon the water-bath until the action was nearly or quite completed. It was found that this completion was greatly facilitated by violent shaking at the moment when the acid was poured upon the cupric oxide, for otherwise the materials inevitably formed a hard cake which dissolved very slowly. In one or two cases a small amount of unchanged cupric oxide was weighed, and subtracted from the original amount.

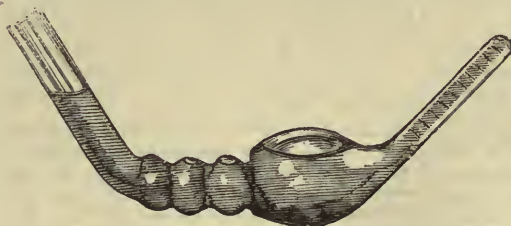


FIG. 2.

The apparent evolution of gas was at first very violent, but this violence might have been partly due to ebullition caused by the heat of the chemical action. The tubes were opened under boiled water or mercury, and the gas was analysed by means of Hempel's apparatus, somewhat modified for accurate use with very small quantities of material. The portion of the gas which was not absorbed by caustic potash, but was absorbed by pyrogallol, is tabulated below as oxygen. The remainder refused to support combustion, suffered no diminution of volume upon the addition of oxygen, and appeared perfectly inert; hence it was undoubtedly nitrogen. In order to test the solution of pyrogallol, analyses of air were made from time to time with satisfactory results. The volumes were of course corrected for temperature and pressure,

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

Occluded Gas in Cupric Oxide.—First Series.

No. of experiment.	Weight of cupric oxide. Grms.	Vessel employed for ignition.	Temperature of ignition.	Vol. of gas evolved uncorr. C.c.	Vol. of O ₂ for 1 grm. CuO. C.c.	Vol. of N ₂ for 1 grm. CuO. C.c.	P.c. of gas in CuO by weight.
58	4'35	Porcelain	Dull red	2'70	0'03	0'59	0'075
59	3'12	{ Double xble Platinum	Bright red	0'30	0'01	0'09	0'012
60	Blank	—	—	0'10	—	—	—
61	1'20	—	Not ignited	3'5 of CO ₂	Trace	Trace	—
62	Blank	—	—	0'10	—	—	—
63	1'20	Porcelain	Dull red	0'73	0'03	0'58	0'073
64	2'20	"	"	1'34	0'03	0'58	0'073
65	2'00	"	"	0'8±	Trace	0'40	0'05±
66	3'20	{ Double xble Platinum	"	1'70	0'05	0'48	0'064
67	2'10	Porcelain	"	1'13	0'00	0'53	0'065

as well as for the tension of aqueous vapour, before the weights of gas were calculated. The conditions varied so little from the mean, 24° C. and 750 m.m., that a statement of these data seems inessential.

The occlusion of an inert gas by cupric oxide was so peculiar a phenomenon that many experiments were needed to carry conviction. Several blank experiments were tried in order to test the freedom of the acid from dissolved air. The fact that only a very small amount of gas was evolved in the second experiment is also valuable evidence upon this point.

The material used in experiments 58, 63, and 64 was four years old, while that used in experiments 59, 65, 66, and 67, had been recently prepared. Both of these samples were made from cupric oxynitrate, whereas the one used in experiment 61 was precipitated by caustic alkali. The tubes of Nos. 64 and 67 were opened under mercury. In No. 64 the cupric oxide was cooled for 48 hours after igniting, while in No. 66 the oxide was still very hot when introduced into the tube.

The series was discontinued because a new method had been devised which was much less tedious and much more direct in its execution. According to the new method, the cupric oxide to be analysed was introduced into a tube shaped in the manner shown in Fig. 2. After the bulbs had been nearly filled with thoroughly boiled warm water, the open mouth of the tube was connected with an air-pump to remove any mechanically adhering air. The water was usually allowed to boil for several minutes under the reduced pressure. The air was then readmitted, and the tube was entirely filled with pure boiled water, being placed perpendicularly for the purpose. When the tube had been returned to its usual position, acid was added through a fine funnel tube in such a manner that it at once attacked the oxide. A short piece of glass rod in the large bulb together with constant agitation prevented the formation of cakes.

In the most carefully performed experiments the sulphuric acid as well as the water was boiled, but repeated trials showed this precaution to be unnecessary. In one blank experiment even ordinary distilled water and sulphuric acid evolved only about one thousandth of a c.c. of gas, while boiled water, which was invariably used in the determinations, gave no trace even of the finest bubbles with unboiled sulphuric acid.

The gas evolved on the solution of the cupric oxide was collected chiefly in the largest bulb. The amount collected in the smaller bulbs decreased in proportion with the increase of distance from the first, and only a very small amount was lost through the open mouth. The gas was measured in the right hand graduated tube, or drawn off for analysis through a rubber connector attached at this end.

The apparatus was afterwards modified to avoid the slight loss through the open mouth. It then consisted of a small stoppered flask with two concentric funnel tubes, and a delivery tube closed with a rubber connector and a pinch cock. When the whole apparatus had been filled with boiled water through the larger funnel tube,

the smaller one was filled with pure sulphuric acid and quickly placed inside the larger one. Upon inclining the flask it is evident that the loss of minute bubbles must have been reduced to a minimum, while the small annular opening between the funnel tubes was quite sufficient to allow the escape of the displaced water. The gas was readily drawn off for analysis through the delivery tube, which just penetrated the smooth rubber stopper.

(To be continued).

SIXTY-FIFTH CONGRESS OF GERMAN
NATURALISTS AND PHYSICIANS.

THIS Congress, first instituted by the illustrious Oken, amidst difficulties arising from the mistaken jealousy of the German governments, now enjoys full recognition from all quarters. Its meeting will this year take place at Nürnberg from the 12th to the 16th of September. The Congress differs in several important respects from its daughter the British Association. It includes not merely "natur-forscher," i.e., men engaged in scientific pursuits, but physicians who of course are, or ought to be, men of science.

The number of sections is thirty-two:—1. Mathematics and astronomy; 2. Physics; 3. Chemistry; 4. Botany; 5. Zoology; 6. Entomology; 7. Mineralogy and geology; 8. Ethnology and anthropology; 9. Anatomy; 10. Physiology; 11. General pathology, pathological anatomy; 12. Pharmacology; 13. Pharmacy and pharmacognosis; 14. Internal medicine; 15. Surgery; 16. Obstetrics and gynaecology; 17. Pædiatry; 18. Neurology and psychiatry; 19. Ophthalmology; 20. Otiatrics; 21. Laryngology and rhinology; 22. Dermatology and syphilis; 23. Hygiene and medicinal policy; 24. Forensic medicine; 25. Medical geography, climatology, hygiene of the tropics; 26. Military sanitation; 27. Dentistry; 28. Veterinary medicine; 29. Agricultural chemistry and agricultural experiments; 30. Instruction in mathematics and natural science; 31. Geography; 32. The knowledge of instruments.

This arrangement of sections, though of course not free from objections, has one signal advantage over that of the British Association,—the absence of the section of statistics and political economy. The Germans do not need to be laboriously told that statistics must rank merely as a method, available in various sciences, but never as an independent science. Political economy, too, wherever introduced, finds an easy transit into party politics.

The Nürnberg meeting is open to foreign *savants*, whose participation will be welcome. The subscription for the session is 12 marks (shillings), but those only who have in addition paid a yearly subscription of 5 marks are entitled to take part in the official deliberations of the Congress and to vote for or against resolutions. Each section is opened by an introductory president appointed by the general committee and then nominates its permanent president.

On Monday, September 12, the Congress is invited by the municipal authorities to a social reunion at 8 p.m. in the Park of the Rosenau Society. The festal banquet takes place on Wednesday, September 14, in the Hotel Zum Strauss, and the festal ball on Thursday, September 15, in the same locality. On Monday, September 12, a general meeting will be held at 9 a.m., at which discourses will be delivered by Professors His, Pfeffer, and Hensen. At 3 p.m. the sections will be opened. On Tuesday, September 13, the sections sit in the morning, and at 2 p.m. the members have the choice of three excursions to Erlangen, to the stalaçtite cavern of Krottensee, or to the præhistoric circular entrenchment Hubërg, near Pommelsbrunn.

On Wednesday, September 14, will be a general meeting, at which papers will be communicated by Prof. Dr. von Helmholtz, Prof. Strumpel, and Prof. Ziegler, and at 5 p.m. ensues the banquet at the Hotel Zum Strauss. Thursday, September 15, will be given up to sectional work, but at 8 p.m. there will be held a ball at the Hotel Zum Strauss.

On Friday, September 16, will be held the final general meeting, when Prof. Günther will discourse on the physical and geographical phase of volcanic phenomena, and Prof. Hüppe on the ætiology of infectious diseases.

Applications for lodgings should be made as early as possible to Herr J. Gallinger (Bergstrasse 8). The number of beds, &c., required should be accurately stated, and it must be noted that attention to applications made later than August 31 cannot be guaranteed.

Applications relating to sectional business should be addressed to the respective secretaries. Other letters (excepting applications for apartments), are to be forwarded to Dr. G. Merkel, Josephsplatz 3. From the names of the *savants* announced as about to take part in the proceedings a most interesting gathering may be expected.

NOTICES OF BOOKS.

Biographical Notice of President Henry Morton, Ph.D., of the Stevens Institute of Technology. Prepared by Prof. COLEMAN SELLERS, E.D., and Prof. ALBERT R. LEEDS, Ph.D. On the Occasion of the Presentation to the Trustees and Faculty by the Alumni Association of a Portrait of President Morton, February 15, 1892.

WE have here a graceful tribute paid by his colleagues and pupils to a *savant* of distinguished merit.

Dr. Henry Morton, President of the Stevens Institute of Technology, is remarkable for his versatility, but we may apply to him the old saying "*nihil tetigit quod non ornavit*." In his career as a student at the University of Pennsylvania he entered with keen interest into literary pursuits, and even took up painting, in which he reached a higher position than that of a mere *dilettante*. In a meeting of the College Philosophical Society he made the daring proposal "that a committee be appointed to translate the inscriptions on the Rosetta Stone, and present the translation to the Society at a future meeting."

This celebrated stone had been already studied by no less authorities than Young and Champollion, though no complete translation had been executed. Mr. C. R. Hale (Dean of Davenport), undertook the Greek and Demotic texts, whilst Morton himself took the hieroglyphic portion in hand. For this purpose he threw himself into the special study of hieroglyphics, and in order to reproduce the designs he acquired the art of lithography. We may here remark that the studies of archæology, of ethnology, and all their accessory disciplines are strikingly popular in America.

After graduating he devoted himself at first to the study of law in the chambers of Mr. G. M. Wharton, of the Philadelphia bar. In 1859, however, he gave up his

legal studies and occupied himself with chemistry and physics. Here we must salute him as an able and successful reformer in higher education. The claims of natural science to a place in the curriculum of Universities not less prominent and honourable than that hitherto monopolised by "classics" or "humanities" were felt in America as early as in Europe. The Episcopal Academy of Philadelphia, one of the preparatory schools of the University, took part in this movement, and young Morton undertook to give some lectures on chemistry and physics which would be interesting to boys. The success of the undertaking went beyond all expectation. "The boys found the novel and brilliant experiments, the clear and entertaining explanations of the facts and phenomena of every day life and experience, so much more entertaining than the derivation of a Greek root, or the history of Remus and Romulus, that the little room in the course of a few weeks became too small for those who wanted to come in." A large and well equipped lecture-room was arranged for the lectures and researches of Prof. Morton. "The new lecture-room speedily became famous, and in the afternoons at extra lectures was crowded with pupils from other city academies, and in the evening with older listeners who were glad to spend a delightful hour in hearing striking expositions of the novel discoveries in physical science."

In 1863 Mr. Morton was elected Professor of Chemistry at the Philadelphia Dental College, and in 1864 he became Resident Secretary of the Franklin Institute.

Among his other successful endeavours to revivify the somewhat decaying Institute he delivered public lectures on reflection, refraction, sunlight, moonlight, eclipses, fluorescence, &c. The general American public seem to take a livelier interest in scientific lectures than is displayed in this country, but this course was rendered especially attractive by the original devices of the author for illustrating his discourses. Even professional men confessed themselves startled by the effects produced. The artificial rainbow, the combustion of a sword from hilt to point, and the illumination of an entire theatre with the monochrome yellow light, the "legions of angels," and the "artificial eclipse" were received with enthusiasm.

In 1868 Prof. Morton accepted as an interim arrangement the Chair of Chemistry and Physics at the University of Pennsylvania, during the absence of Prof. J. F. Fraser. On his return the department was divided and a new Chair of Chemistry was created and was accepted by Prof. Morton. About this time he discovered the nature of the bright line seen on the sun's disk near the edge of the moon during partial eclipses (see *CHEMICAL NEWS*, vol. xx., p. 313).

In 1870 Prof. Morton resigned the secretaryship of the Franklin Institute and accepted the Presidency of the Stevens Institute. In 1878 he accepted a position as Chairman of the Committee of Scientific Tests in the Lighthouses Board of the United States, vice the late Prof. Joseph Henry. He has long been recognised as the foremost scientific expert in New York in patent litigations and in similar cases. It must be remarked that in the United States, despite the careful examination instituted before granting a patent, disputes as to the validity, the proprietorship, and the scope of a patent, seem not less frequent than in Britain.

We do not know whether the attention of Prof. Morton was ever drawn to the necessity of altering the present system of taking scientific evidence, and of making the expert the assessor of the Court, instead of the witness "called" by either party and treated by the other as a kind of informal advocate.

The scientific researches of Prof. Morton have been numerous and important, and would have been largely multiplied had not so much of his time been occupied by his official duties.

Foremost must come his investigation of the fluorescent and absorbent spectra of the uranium salts. For the

details of this research the reader must be referred to the *CHEMICAL NEWS*, vol. xxviii., pp. 47, 113, 169, 233, 244, 257, and 268; and vol. xxix., p. 17. In 1872 and 1873 followed a series of investigations on the fluorescent relations of anthracene, pyrene, chrysene, and a new solid hydrocarbon (thallene) found in petroleum distillate (see *CHEMICAL NEWS*, vol. xxvi., pp. 199, 272, and vol. xxxiv. p. 188). Concerning the value and the importance of these researches we need merely mention their appreciation by Sir G. G. Stokes, of Cambridge, and by Dr. Tyndall.

Prof. Morton's attention was given to a considerable extent to the development of the magic lantern as a means of illustrating lectures. An account of his improvements will be found in the *CHEMICAL NEWS*, vol. xxix., p. 92, and vol. xxv., p. 251.

A paper which appeared in 1879 (*CHEMICAL NEWS*, vol. xxxix., p. 255), treats of "the chronology of the isomeric purpurines and the actual relations of some of the bodies which have been called anthrapurpurine, isopurpurine, and flavopurpurine." There seems good reason to conclude that he was the first to isolate and recognise flavopurpurine.

Other published researches relate to the elimination of antimony from the human system, to the measurement of incandescent lamps, and to so-called water-gas. He is one of those who eschew the error of explaining physical facts by ultra-human agencies. At the same time, as we may be pardoned for remarking, and as he shows very ably in a paper on "The True Relations of Physical Science to Religion" (Stevens's "Indicator," 1888, vol. v., p. 158), he insists that science and religion can neither directly support or refute each other.

It is interesting to note that whilst Prof. Morton is highly esteemed as an original investigator, as a lecturer, and as an educational organiser, he is no less appreciated among a wide circle of friends, among his colleagues and pupils, for his unvarying courtesy and kindness.

The illustrations of this book are beautiful, whether they display fluorescent spectra, photographic views of lunar scenery, or fanciful designs.

We hope that Prof. Morton may long survive to exert his varied talents and to promote the scientific culture of his country.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiv., No. 26, June 27, 1892.

Contribution to the Study of the Function of Camphoric Acid.—A. Haller.—M. Friedel ascribes to the molecule in question the threefold function of a carboxylic acid, a ketone, and an alcohol, whilst the majority of authors who have occupied themselves with this substance consider it as a dicarboxylic acid. These differences of opinion bear merely upon the constitution of the nucleus C_8H_{14} .

On Aluminium.—M. Balland.—Towards the end of last year H. H. Lubbert and Roscher announced that aluminium was attacked by wine, brandy, coffee, and tea, and was consequently not a fit material for field flasks or other vessels of the same kind. The news propagated by the press has caused doubts as to the future of this metal, doubts which have been shared by the War Department. The author has undertaken numerous experiments to check the assertions of the German chemists. The material employed was sheet aluminium produced in France, of the quality met with in trade. It is 1 m.m. thick and weighs 27.75 grms. per square deci-

metre. For these trials plates were taken of 5 grms. in weight, measuring 18 square c.m., and presenting a surface very close upon 38 square c.m. These plates before being put in use were cleansed with all desirable care, as were also the vessels employed. It results from our experiments, which were pursued for some months, that aluminium may be employed with advantage in the manufacture of utensils for domestic use. Air, water, wine, beer, cider, coffee, milk, oil, butter, fat, &c., urine, saliva, soil, &c., have less action upon it than upon the common metals (iron, copper, lead, zinc, tin). Vinegar and common salt indeed attack it, but in proportions which should not interfere with its employment. It loses in vinegar in four months only 0.349 grm. per square decimetre, and 0.045 grm. in 5 per cent solutions of salt.

Action of Chlorine upon the Alcohols of the Fatty Series.—A. Brochet.—In this paper the author studies the chlorisobutylic paraldehyd a , $C_{12}H_{21}Cl_3O_3$.

On Asboline (Pyrocatechine and Homopyrocatechine).—M.M. Béhal and Desvignes.—Asboline is a substance which Braconnot obtained from the soot of wood-smoke, and which he regarded as a definite nitrogenous compound. The author has resolved it into two portions, $C_6H_6O_2$ and $C_7H_8O_2$.

On Vegetable Cholesterines.—M. Gérard.—The cholesterines extracted from phanerogamous plants have all the physical and chemical characters of Hesse's phytosterine. The cholesterines extracted from cryptogamous plants give the same reactions as Tanret's ergosterine. Tanret indicates the following differential reaction. On treating a small quantity of phytosterine with concentrated sulphuric acid, the phytosterine takes a reddish brown colour and dissolves incompletely. If chloroform is then added to the mixture the latter takes a yellow colouration, which soon turns to blood-red and to violet. Animal cholesterine gives the same reaction. On the contrary, ergosterine dissolves completely in concentrated sulphuric acid, and if chloroform is added to the mixture it remains colourless. Cholesterine has been extracted from the lupin, from fœnugreek, from the seed of *Datura*, and from olive oil. Among the lower plants the author has obtained it from *Æthaliu septicum* and *Penicillium glaucum*.

Researches on the Falsification of Essence of Santal-Wood.—E. Mesnard.—By using pure ordinary sulphuric acid it is easy to ascertain if an essence of santal is pure or if it is mixed with essences of cedar, cubebs, copaiba, turpentine. In the former case the reagent gives a viscid liquid which becomes a paste, and is rapidly transformed into a solid mass adhering very strongly to the glass. This mass is easy to recognise by its light grey-blue or greyish colour and the dusty aspect which it assumes with age. In the second case the resinous mass does not solidify entirely and always retains a deep colour with a very distinct lustre.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 9.

Nitroketone derived from the Camphosulphophenols.—P. Cazeneuve.—The author has examined the potassium, ammonium, calcium, barium, copper, lead, and silver derivatives of this compound, as also certain alkaloidal derivatives.

Action of Hydriodic Acid upon Carbon Tetrachloride.—B. Walfisz.—This is a case of the formation of iodoform without the presence of an alkali, and setting out from a derivative of methane.

Study of the Azo- and Alkylidene Derivatives of Chrysaniline as well as of the Colouring Substances thence Derived.—A. Trillat and de Rackowski.

Decomposition of Silver Permanganate and a peculiar Association of Oxygen with Silver Oxide.—A. Gorgen.—Already noticed.

THE CHEMICAL NEWS.

VOL. LXVI., No. 1705.

THE CENTRIFUGAL EMULSOR.

By MARTIN EKENBERG.

By the aid of this machine uncongenial fluids, as for instance oil and water, may be caused to mix mechanically most intimately. In consequence of its continuous work and productive power, the emulsor substitutes most satisfactorily stirring or other means of bringing about a mixture used in the tar industry, soap manufacture, &c. For the benefit of those who do not know the emulsor I will describe it before entering upon the experiments I have made with it.

The apparatus is very simply and substantially made, and easily managed when in use; it consists of two massive plates, turned towards each other, and fastened upon a vertical axle (see Fig.). The plates rotate with a rapidity of 6 to 7000 revolutions per minute. The opening between them may be increased or diminished from 0.05 m.m. to 1—2 m.m. By the size of this opening the grade of oil in the emulsion is regulated. If the opening be small, 0.05—0.01 m.m., a very fine emulsion is produced,—for instance, from olive oil and water. In this case the oil globules are much smaller than those in milk. From such an emulsion the fat is separated by gravity within 20 to 25 minutes, but if the water be alkaline the emulsion remains for a longer period. A larger opening produces a less fine emulsion, which separates itself in much shorter time, say in 2 to 3 minutes, if the opening be 1 m.m. The quantity produced is in proportion to the size of the opening, and varies from 300 to 2000 litres per hour. Previous to the making of an emulsion all mechanically introduced hard and coarse particles which cannot pass through the opening must of course be separated by filtering. Emulsions containing as much as 40 per cent of oil may be made, even up to 50 per cent of certain oils. On the other hand, one may mix five, ten, or even thirty per cent of water with the oil; consequently there is a limit for the emulsive process in reference to the quantitative proportions of the mixtures. Emulsions of water in oil become valuable when small quantities of salts or other agents in solutions of water are desired to act on the oil. The consumption of agents may in this way be reduced to the smallest possible quantity. Emulsions of water or salt solutions in oil made by the emulsor have several interesting qualities, of which I hope to speak further in a future article. The emulsor may be used either in an ordinary separator frame with a pulley (see Fig.), or else in a steam turbine frame, the latter being the most handy, as the machine will work simply by turning a steam valve.

The plates of which the emulsor consists are made from strongly tinned Swedish iron, or from iron with a preparation of antimony and lead, or from acid proof bronze: which material will be chosen depends upon the purpose for which the machine is intended. The plates may easily and inexpensively be replaced by new ones when worn out, which can only take place after a long and continuous use. Should they become rough from the action of acids, &c., they may simply be ground and tinned with antimony and lead, which will render them equal to new; and this operation may be repeated a great number of times on account of their extreme massiveness. Emulsor plates of Swedish iron are always used for acid emulsions in cases where small quantities of iron in the cleansing water do not harm the product. When used for alkaline emulsions and washings with water the plates will prove to possess great durability.

All other parts, frame, &c., are equally solid and con-

structed on the same principles as the "Alpha" milk separators.

The following is a brief account of experiments made by me for the purpose of ascertaining the fitness of the machine for the object intended, namely, intimate mixing of uncongenial liquids. The experiments are made with quantities varying between 50 and 300 kilograms.

SERIES A.—Washing away of Free Mineral Acids from Oils and Fat.

From Olive Oil.—To common machine oil I added 5 per cent of sulphuric acid of 1.50 specific gravity, and mixed this sour oil in water in such a way that an emulsion of about 20 per cent of oil was obtained. The opening between the emulsor plates was about 0.1 m.m. The emulsion separated itself in 10 to 15 minutes. After one more washing with fresh water the oil was free from acids, which was tested with litmus paper, after having shaken the oil with warm distilled water. The oil was at first not clear owing to the presence of air bubbles and drops of water, which all disappeared after the oil had stood for 24 hours undisturbed. One part of the oil was obtained free from water and air immediately, by filtering through newly burnt sulphate of lime.



CENTRIFUGAL EMULSOR IN SECTION.

The oil may be separated easily from the washing water with a receiver constructed on the principle of the Florentine flask, and capable of holding that quantity of emulsion, which is made in the time required for the oil to separate itself from the emulsion.

The washing-water contained in the above mentioned cases a small number of minute particles of oil; these could easily be collected in either of the following ways:—

1. By filtering through cotton-wool and boiling the wool in water, when the oil rises to the surface.
2. By leaving the washing-water undisturbed for about 48 hours, when all the oil will float on the top.
3. By mixing more olive oil with the washing-water and using a large opening. The large oil globules hereby produced brought the smaller ones with them to the surface and a clear washing-water remained. This way of separating minute particles of oil from the washing-water is very effective; even from alkaline washing-water could all oil be re-claimed by using mineral oil.
4. By centrifugal power in continuous oil separator with the same rapidity as the emulsor.

As I have shown, there was no difficulty in extracting the whole of the oil from the emulsion.

At a repeated experiment with olive oil, when 5 per cent of sulphuric acid of a specific gravity of 1.84 was used, all free sulphuric acid was washed away in two washings, one with warm and one with cold water. In this case, however, the oil was strongly affected by the acid.

From Tallow.—Raw tallow was melted and about 3 per cent of nitric acid was mixed into this. After two washings with water I got a pure, light, acid-free product. When the tallow had separated itself from the emulsion all cell fragments, &c., stayed underneath the pure tallow

as a well-defined layer. This way of separating membranes, loosened by the action of the acid, seems to come in very handy for refining tallow.

From Mineral Oils.—In a lubricating oil of a brownish colour I mixed 5 per cent of sulphuric acid of 1.84 specific gravity. The oil was then washed twice with water; the first washing-water had taken up much colouring matter. After a third washing with concentrated solution of caustic soda, I got an oil which had only a slight yellowish tint.

In another experiment I took raw vaseline from Galicia, melted it, and with help of the emulsor I mixed into it about 5 per cent concentrated sulphuric acid and some chromate of potassium, washed the vaseline with warm water, and then filtered it through a layer of bone-black ro c.m. thick (to get rid of carbon particles and newly formed brown colouring-matter), and by this process I got an almost colourless vaseline.

SERIES B.—Washing away of Free Fatty Acids from Oils.

From Olive Oil.—I mixed the oil with water containing 0.5 per cent of caustic soda. The oil extracted from this emulsion was then washed in clean water and lastly in water with some sulphuric acid. After this process the oil was free from fatty acids.

Out of the first washing-water, which contained soap, a liquid fat consisting principally of fatty acids separated itself when acid was added.

From Hemp Oil.—This oil was treated in the same way, and was also made perfectly free from fatty acids.

SERIES C.—The Use of the Emulsor in Manufacturing Soap.

a. *Cocoanut oil* was mixed with a strong solution of caustic soda. This emulsion, already containing a great deal of fat in a saponified condition, yielded immediately on boiling a homogeneous soap.

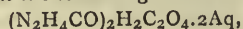
b. *Cocoanut oil* was warmed up to about 110° C. and then mixed with a solution of caustic soda at boiling-point. The result was a liquid containing a number of gas bubbles which caused an opalescence and hardened when cold. On examination it was found to contain no free fat, so that a perfect and almost immediate saponification had been obtained.

Results of later experiments with the emulsor in saponification of fat with sulphuric acid, washing of tar, &c., I intend to publish at an early date.

NOTE ON THE FORMULA OF UREA OXALATE.

By PATRICK H. KIRKALDY.

HAVING occasion to determine the carbon and hydrogen in urea oxalate, I found, on reference to "Bloxam's Chemistry," that the formula given was—



which gave the following percentages:—

Carbon .. 19.512 Hydrogen .. 5.691

The result of my first analysis of the oxalate, obtained by precipitation from a hot solution, was—

Carbon.. 22.16 p.c. Hydrogen.. 4.903 p.c.

which pointed to the supposition that the body was anhydrous, in which case the calculated percentages are—

Carbon .. 22.85 Hydrogen .. 4.76

A second analysis was then made of crystals obtained by allowing the mother-liquor to stand, when the results obtained were—

Carbon.. 23.04 p.c. Hydrogen.. 5.126 p.c.

A third analysis of some of the first crop of oxalate

crystals dissolved in as little water as possible and re-crystallised *in vacuo* gave the following results:—

Carbon.. 22.804 p.c. Hydrogen.. 4.787 p.c.

In order to further check the results I made two determinations of nitrogen in the re-crystallised oxalate. The calculated percentage in the anhydrous body is 26.67.

The results obtained from the re-crystallised product were—

(1) 27.38 } Mean, 26.94.
(2) 26.51 }

In conclusion, 1.3125 grms. of the air-dried re-crystallised oxalate were left *in vacuo* over H_2SO_4 for sixteen hours; no change in brilliancy took place, and only a slight loss in weight, amounting to 0.4 per cent.

0.659 of a gm. was left in a water-oven for two hours. The loss in weight resulting was only 5 m.grms., or 0.76 per cent, probably due to the partial decomposition of the body. It appears, therefore, from the results of analysis that urea oxalate is an anhydrous salt.

	Found.	Required for (N_2H_4CO) $_2$ $H_2C_2O_4$.
Carbon	22.804	22.85
Hydrogen	4.787	4.76
Nitrogen	26.94	26.67
Oxygen	—	45.72
		100.00

The following books make no mention of water of crystallisation:—"Watts' Organic Chemistry," "Miller's Elements of Chemistry," "Watts' Dictionary," "Dictionnaire de Chimie," by Wurtz, and "Cours de Chimie," by Gautier.

The following state that urea oxalate crystallised with 2Aq:—"Bloxam's Chemistry" and "Strecker's Organic Chemistry," while in "Booth and Morfit's Chemistry" the following formula is given:— $C_2H_4N_2O_2 + C_2O_3 + HO$, in which there seems to be some error.

Chemical Laboratory,
King's College, London, W.C.

THE CHANGE OF PRESERVED FERRUGINOUS MINERAL WATERS.

In a recent note (*Comptes Rendus*, cxiv., 1363), M. Parmentier very rightly emphasizes the well-known fact that mineral waters away from the spring undergo a change in the vessels which contain them, and he proposes a method for their better preservation. He says:—

I am not aware whether any experiments have been made which give an idea of the degree of change which takes place in transported mineral waters. It is, as we know, variable; but some years ago I had an opportunity of examining some ferruginous mineral waters from the point of view of their iron contents, and it is the result of these experiments made by a rapid method which I intend to state.

In order to be as much as possible in the ordinary conditions of therapeutic employment of these waters away from the spring, I took them in bottles from one of the best chemists of Paris. The vessel placed standing during the very short time requisite for the ferruginous deposit or that of other substances in suspension, is carefully opened, and 250 cubic centilitres of the limpid part is syphoned, where, immediately after acidification, the iron protoxide is estimated with a weak solution of permanganate, in accordance with the well-known prescriptions. In a second similar quantity tested, the total amount of iron is found after reduction by zinc and the same reagent.

This rapid procedure, so convenient and frequently employed for determining small quantities of iron, is not perhaps in this case quite free from reproach, on account

of the possible presence of organic or sulphurous substances in some mineral waters. But we know that in the cold the decolouration of permanganate by ferrous salts is instantaneous, whilst it is slow and progressive for most of the organic substances; this second phase of the operation serves even to verify its presence. Let us also observe that the action of organic substances tends to increase the amount of iron, but in this case the figures obtained would show *à fortiori*, as we shall see, that the iron dissolved has almost disappeared in most of the transported mineral waters.

The results of the experiments have been calculated in metallic iron, in solution, in a litre; this form is beyond all dispute and permits later hypothetical groupings. The results, besides, are placed opposite the metallic iron contained in a litre calculated according to the analyses of waters drawn from the spring, which are to be found in special publications.

Transported Mineral Water.

	Metallic Iron.		Water taken at Spring.
	Dissolved in state of protoxide. Grm.	Total after reduction by zinc. Grm.	
Auteuil	0.0007	0.0022	0.0809 (O. Henry père)
Busang	0.0000	0.0007	{ 0.0082 (O. Henry)
Forges (Royale) ..	0.0000	0.0007	{ 0.0041 (Willm)
„ (Reinette) ..	0.0002	0.0010	0.0521 (Girardin & Morin)
Lamalon (Bourges)	0.0002	0.0059	0.0171
Orenna (Sorgenta)			0.0050 (Bechamp)
Sotlana)	0.0000	0.0011	0.0618 (Poggiale)
„ (2nd example)	0.0000	0.0004	0.0618
Pougues (St. Leger)	0.0004	0.0015	{ 0.0072 (O. Henry)
Soultzbach (Alsace)	0.0000	0.0000	{ 0.0021 (Carnot)
			0.0112 (Oppermann)
Spa (Poutron). ..	0.0255	0.0260	0.0448 (Monheim)
Vals (Rigollette) ..	0.0002	0.0015	?
Vichy (Lardy) ..	0.0004	0.0011	0.0073 (Willm)

One can see from these few examples that most of the waters considered ferruginous lose, according to the present system of preservation, either all or most of their iron, which is precipitated, and the small amount which remains in solution is in the ferric state. It results that in many of the cases in question, and considered (to the exclusion of other principles) as a ferruginous re-constituent, the results may become unreliable from the therapeutic point of view, and some improvement in the method of preservation is necessary. Specialists have for a long time been studying this preservation, as shown by the numerous articles devoted to this subject in works on hydrology. It has been proposed to fill the vessels with a dipping tube, and expel the air by inert gases, chiefly carbonic acid (M. Porret). Some mineral waters are even surcharged with this gas. This last practice is not advisable, because it changes the nature of the water drawn from the spring.—*Comptes Rendus*, June 20, 1892.

Plumbiferous Glass-Wool.—L. Blum.—In the course of gas-analytic operations the author caused gases containing sulphuretted hydrogen to traverse a plug of fine white glass-wool, as obtained in commerce. The wool was blackened, and on further investigation it appeared that the blackening was due to the formation of lead sulphide. Hence a plumbiferous glass had been used for the production of the glass-wool. In various analytical operations where glass-wool is used the presence of lead is objectionable. Nor can such material be used, as recommended, for filtering acids, since they may become contaminated by taking up lead.—*Zeitschrift für Anal. Chemie*, xxxi.

THE EFFECT OF LIMING ON THE POROSITY OF CLAY SOILS.

By A. N. PEARSON,
Chemist for Lands, Agriculture, and Victorian Water Supply.

WHILE reporting recently on the site proposed for the establishment of a sewage farm in connection with the sewage scheme now being carried out by the Melbourne and Metropolitan Board of Works, I was led to consider how the porosity of the soil might be increased, the soil in many parts being a stiff clay. The amelioration of clay soils by means of liming is an old agricultural expedient, hence it occurred to me to ascertain definitely how much the porosity of clay soils was improvable by liming.

In testing the permeability of soils, certain precautions must be adopted, otherwise exceedingly discordant results will be obtained. The precautions I took were as follows:—The soils were all dried to the same degree of dryness, and were afterwards ground and sifted to the same degree of fineness. Care was taken that the soils in the different percolation tubes were compressed to the same degree of compactness; to this end the tubes, when being filled, were all inclined at the same angle, as shown at A in the diagram, so that in each case the soil ran down the side of the tube with the same velocity. The soil was filled up after two or three trials to $\frac{1}{4}$ inch above the mark, then the tube was slowly raised to an upright position, suspended between the finger and thumb of one hand, and gently tapped from below with the finger of the other hand, until the soil sank down exactly to the mark. It was found impossible to pour water down the tube even in a very fine stream without disturbing the surface of the soil. But any disturbance of the surface of clay causes a difference of porosity. To obviate this difficulty I covered the clay with a layer, $\frac{1}{4}$ -inch thick, of sand of uniform size. The water was run into the tubes by means of a water-bottle arranged as shown at B in the diagram, the delivery tube having attached to it a piece of indiarubber tubing acting as a syphon and furnished with a screw pinch and with a fine delivery jet. By this means the water could be delivered in the gentlest stream. With these precautions results were obtainable sufficiently accordant for my purpose.

The test adopted was to pour two inches depth of water on to two inches depth of dry soil, and to observe the time required for the water to disappear below the surface of the sand.

The differences in the time required with different soils were very great, as will be seen from the following examples:—(See Table I.).

To observe the effect of liming I mixed samples of the dried and sifted soils with $\frac{1}{2}$, $\frac{1}{4}$, and $2\frac{1}{2}$ per cents of quick-lime, then added water, worked into a paste, dried, ground up, and sifted, and tested for percolation as before. The results obtained are given in Table II.

It is certainly noteworthy that a soil such as No. 3, which in its natural state required from twenty-three to thirty-one days for two inches of water to percolate through it, allowed the water to pass through in an average of seven hours after the soil had been mixed with $2\frac{1}{2}$ per cent of lime. Perhaps, however, the most striking case is that of Sample No. 1, which in its natural state required six days four and a quarter hours for the water to pass through it, but when mixed with only a quarter per cent of lime required only twelve and three-quarter hours. Had the test consisted of pouring two inches of water on to wet soil instead of on to dry, the contrasts would have been still greater.

The application of lime to the soil of sewage farms situated in clay districts might be useful for more reasons than one; it would reduce the area required, render underground delivery possible where otherwise impossible, and probably assist materially in the purification of the sewage.

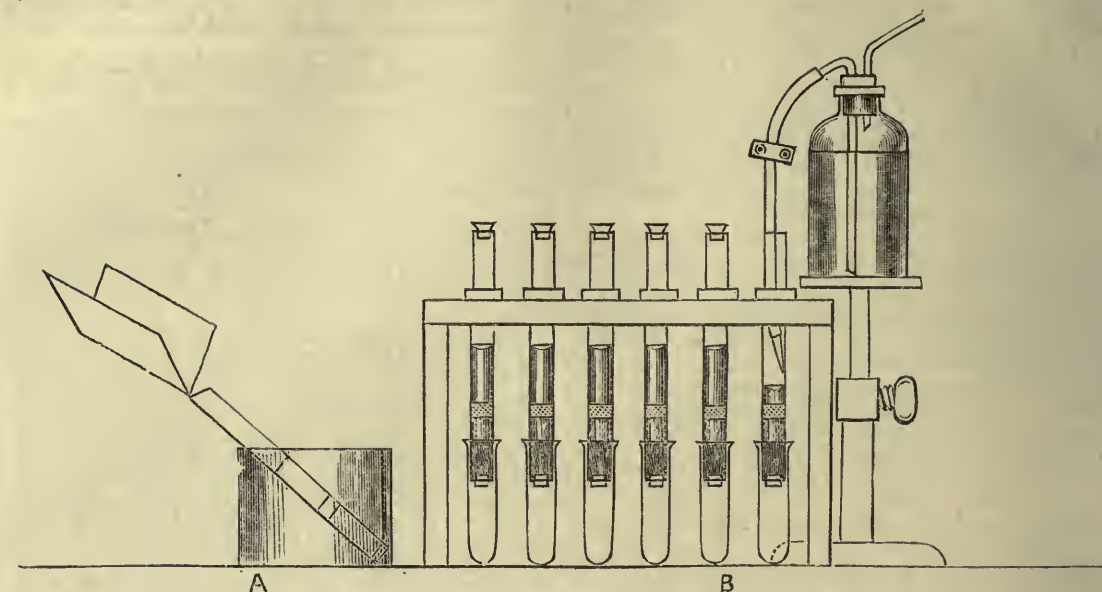


TABLE I.—Time Taken for Two Inches of Water to Pass Through Two Inches of Soil.

Adelaide Sewage Farm.		Pentridge Sewage Beds.		Werribee Delta, N.E. side.	
Sandy side, 1—2 ft. deep.	Clay side, 1—2 ft. deep.	Old beds, 0—1 ft. deep.	New beds, 1—2 ft. deep.	0—17 inches.	17 inches to 4 ft.
2½ mins.	18 days 13½ hrs.	3 hrs. 22 mins.	15 hrs. 12 mins.	18 mins.	28 days 18 hrs.
2 "	14 " 4 "	2 " 55 "	14 " 43 "	22 "	29 " 10 "
Aver. 2½ mins.	16 days 8¾ hrs.	3 hrs. 23½ mins.	14 hrs. 57½ mins.	20 mins.	29 days 2 hrs.

TABLE II.—Table Showing Difference in Rate of Percolation Due to Liming the Soil.

Sample No. 1.			
Soil only.	Soil with ¼ per cent lime.	Soil with ½ per cent lime.	Soil with 2½ per cent lime.
4 days 2 hrs. 30 mins.	11 hrs. 20 mins.	10 hrs. 0 mins.	2 hrs. 0 mins.
7 " 5 " 0 "	14 " 5 "	9 " 53 "	3 " 50 "
7 " 5 " 20 "			
Aver. .. 6 days 4 hrs. 17 mins.	12 hrs. 42 mins.	9 hrs. 56½ mins.	2 hrs. 55 mins.
Sample No. 2.			
13 days 2 hrs. 23 mins.	10 days 8½ hrs.	5 days 2 hrs.	7 hrs. 39 mins.
10 " 3 "	9 " 21 "	5 " 11 "	9 " 0 "
14 " 5 "			
Aver. .. 12 days 11 hrs. 28 mins.	10 days 2¾ hrs.	5 days 6½ hrs.	8 hrs. 20 mins.
Sample No. 3.			
23 days 5½ hrs.	7 days 10½ hrs.	2 days 14½ hrs.	5 hrs. 20 mins.
25 " 21½ "	8 " 12 "	2 " 10¾ "	8 " 40 "
31 " 6½ "			
Aver. .. 26 days 19 hrs.	7 days 23¼ hrs.	2 days 12½ hrs.	7 hrs.

I may be allowed to conclude parenthetically by saying that inasmuch as sewage does not constitute a well-balanced manure, but is relatively deficient in phosphoric acid, sewage farms, unless their soils are specially rich in phosphoric acid, should be manured with bone meal or Thomas slag meal, otherwise the crops raised on them will not be of normal and perfectly sound growth. The Thomas slag meal would to a slight extent serve the purpose also of liming.

Melbourne, June 10, 1892.

Probable Presence of Iron Carbonyl in Certain Kinds of Coal-Gas.—M. Guntz.—Facts observed near Nancy show that the gas has contained iron since the gas-works began to use a purifying mixture containing iron.—*Bull. de la Soc. Chim. de Paris*, vii., No. 10.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, July 12th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the

mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, eleven were found to be very slightly turbid; the remainder being clear, bright, and well filtered.

It will be seen from the Tables that, owing doubtless to the occasional stormy rainfall of the month, several of the samples of water examined had to be described as "very slightly turbid," an expression made use of to signify such a deficiency in brightness as is recognisable only on careful examination. In other respects the entire number of samples examined were found to be of excellent quality, especially in regard to their maintained freedom from colour-tint and excess of organic matter. Thus, taking the Thames-derived samples for comparison, the mean proportion of organic carbon was found to be 0.107 part in 100,000 parts of the water, as against a mean of 0.119 part for the previous month; while the maximum amount of organic carbon in any single sample examined was found to be 0.134 part, as against a maximum for the previous month of 0.143 part, the insignificant differences in amount, or 0.012 part and 0.009 part respectively, being to that extent in favour of the June supply. The mean proportion of organic carbon present in the Thames-derived samples examined during the past half-year terminating on June 30th amounted to 0.131 part in 100,000 parts of the water, corresponding to less than a quarter of a grain of organic matter per gallon.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

APPARATUS FOR WASHING PRECIPITATES.

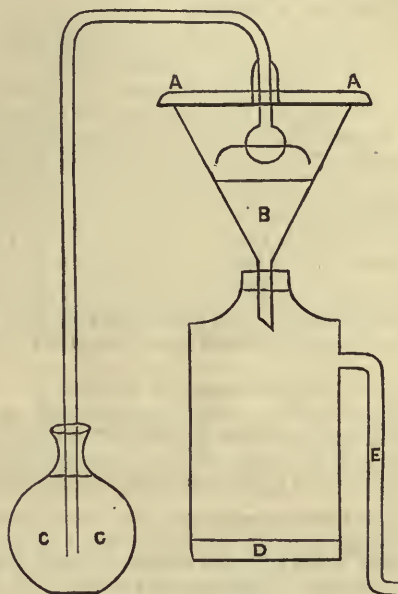
By MATTHEW FORBES.

THE following simple apparatus for the washing of precipitates will be found to be of much advantage, especially when washing gelatinous ones:—

Procure a lead disc about $\frac{1}{2}$ inch thick and a little larger than the funnel that is used, with a true face and a projection on the centre of the other side, with a hole bored through ($\frac{1}{8}$ inch) to admit of a piece of glass tubing passing easily through; then blow a small bulb on one end of tube, and pierce four small holes with a needle through the side of it while held in the flame; then get a disc of the thinnest indiarubber and punch a hole smaller than the glass tubing, and pass tubing through both discs and projecting beyond the other side, and slip on a piece of indiarubber tubing to embrace both glass tubing and projection on lead disc; and to the other end of rubber tubing connect a convenient length of tubing to be led into a flask or jar of the washing fluid to be used. Now throw precipitate into funnel with ground face and wash it down on filter paper as much together as possible, and leave a little more fluid in funnel than you wish to have during washing. Now moisten the discs with water, and place on funnel, pressing firmly down and round a little, and start filter pump; the result of which will be that as the fluid is withdrawn from funnel the washing fluid in flask will pass over to replace it (if all the joints are air-tight),

and will now wash as long as you choose simply by keeping flask supplied with washing fluid, and leaving one free to work at something else.

The apparatus washes very quietly and does not disturb the precipitate, the fluid acting more as a series of layers of fluids passing through precipitate.



A, Lead and rubber discs
B, Precipitate and fluid.
C, Washing-fluid.
D, Filtrate.
E, Tube leading to filter pump.

In the event of the small bulb dipping into the fluid in funnel, lift out tubing from the flask before stopping filter-pump, as otherwise some of the precipitate might be carried back to flask when filter-pump is stopped.

The accompanying sketch will give a clear idea of the apparatus.

ON NATURAL PHOSPHATES.*

By J. LAINSON WILLS, F.C.S.

(Concluded from p. 47).

Nodular, Concretionary, and Arenaceous Phosphates.

THESE are by far the most important of nature's phosphatic reserves, comprising as they do the South Carolina deposits, the French deposits of the Somme, Ardennes, and Meuse, the Belgian fields of Mons and those more lately opened up at Liege (Hesbaye). The so-called "Bordeaux phosphates," because being formerly shipped from that port, but having their real origin in the region of Quercy, comprising portions of the departments of the Lot, Tarn, and Garonne, and Aveyron, also furnish a considerable quantity of nodular or phosphatic concretions of kidney shape, of great purity (88 per cent), and curious geological interest. These are well represented by specimens on the table, and coming from the crevices in the Oolitic limestones, accompanied by *débris* of Tertiary age (Eocene), the walls of the crevices or fissures being at the same time incrustated with phosphorite of a high degree of purity, attaining 80 per cent of tribasic phosphate of lime.

We must not omit here the Florida nodular beds of land and river formation, which are now enjoying such a glorious boom.

As a peculiarity of this Bordeaux phosphorite, we may mention that it contains a very appreciable proportion of iodine.

The Russian deposits, situated between the rivers Desna and Don, occur in the Cretaceous system, at about the same horizon as the Cambridgeshire coprolites, and may be described as nodular.

The Nassau or Lahn concretions in clay are of Tertiary age, and although not exhibiting signs of organic remains, are generally believed to be of animal origin; they attain 60 to 75 per cent phosphate of lime, but are too ferruginous to be much in request for superphosphate manufacture.

The Belgian (Ciply) deposits, which have furnished over 150,000 tons per annum of a 40 to 50 per cent product, are of a nodular character, although the grains are often so fine as to be considered more correctly arenaceous.

The same may be said of the very remarkable French deposits, discovered near Amiens in 1886, and known as the Somme phosphates. These are granular or arenaceous, and to this feature, as well as to their richness (65 to 80 per cent), may be attributed the enormous development which they have enjoyed in such a short period, attaining the annual production of 200,000 tons.

Conglomerates and Breccias.

Phosphatic beds may also assume these characters sometimes with the cementing material as the phosphatic element, and at others with the enclosed pebbles or angular fragments as the valuable portion for commercial supplies.

Thus the Cambridgeshire coprolite fields furnish a conglomerate of phosphatic nodules, cemented by ferruginous sand, while in the Ardennes district (France), is found a peculiar agglomeration of granules of chlorite in a phosphatic cement, the whole yielding 40 to 45 per cent phosphate of lime.

The Belgian (Ciply) deposits yield abundant supplies of a mass of phosphatic nodules, shells, casts, and fossils, cemented in a calcareous matrix, to utilise which has puzzled the ingenuity of many an "exploitant."

Phosphatic Limestone and Marls

Are found in most strata from the Silurian epoch down to more recent time.

The metamorphosis or transmutation of earthy carbonates into phosphates is a very simple and comparatively rapid process, and the evidence of Dr. R. Ledoux in the following description is instructive. He says in a recent article on phosphates: "Some clients of mine sent a ship to a coral island in the Southern Pacific to bring away a cargo of bird guano. The birds were still in countless thousands. The captain had been there for a load twenty years before, and since that time no guano had been removed. At his first visit the crew had cleaned off a space and made a house of coral rock, covering it with a sail, and had used it for a shelter and storehouse while at work. On leaving, the sail was taken away and the walls and board floor left. On the return, twenty years after, there was an average depth of twenty inches over the floor—an inch a year. The underlying limestone was altered into phosphate for a depth of several feet, but the conversion of carbonate into phosphate gradually became less perfect as depth from surface was attained."

I have observed the same effect myself taking place in the West Indies, where the surface of the coral rock is speedily converted into phosphate of lime, wherever the sea-birds are in the habit of congregating.

Such indeed is the simple origin of some of the most important deposits of phosphate in that portion of the world, *i.e.*, Curacao, Sombrero, and Aruba, &c.

The prospecting and first development of the latter named island having fallen to my own care and experience, I am able to produce some interesting specimens here, illustrating very clearly the history of their formation, by examination of their fossil organisms, originally carbonate

of lime (coral rock), and now seen to be, by analysis, phosphate of lime of over 80 per cent.

The deposits of Florida and South Carolina would appear to owe much of their phosphatic wealth to *débris* of phosphatised limestones and marls.

One of nature's operations, which is a factor in enriching already formed phosphate beds, may be here alluded to, namely, the property of spring waters (which often contain considerable proportions of bicarbonates and free carbonic acid) to dissolve neutral carbonate of lime, even when presented to them in apparently as the most compact and impervious material. Such has been the origin of the many remarkable caves existing in the limestone rock formations (Cheddar, Derby, Kentucky, &c.).

This property applied to a calcareous phosphated material will, in course of time, ablate, as it were, more carbonate than phosphate, and to this action is attributed the value of many thousand tons of material, in such extensive beds as those of the Somme, Ciply, Liège, and probably of Florida.

While speaking of these beds of the Cretaceous period, I may mention the recent opening up of another similar field in France. I refer to that in the department of the Pas de Calais, which would appear to be of the same nature as that of the Somme.

Apatites.

Although crystallised phosphate of lime is found as a component of rock masses in more recent strata, yet we do not yet know of any workable deposits of this mineral before passing to the oldest of fossiliferous systems, the Laurentian.

The rocks of this formation are among the most ancient on the North American continent and probably correspond to the oldest gneiss of Scandinavia. The modes of occurrence are so varied in the Canadian apatite field, that the subject would require to be treated by itself in order to do it justice here.

We are all here familiar with how it is found, both in Ontario and Quebec provinces.

Dr. Hunt thus describes, in 1884, the main features of its mode of occurrence:—"The deposits of apatite are in part bedded or interstratified in the pyroxenic rock of the region, and in part are true veins of posterior origin. The gneissic rock with their interstratified quartzose and pyroxenic layers, and an included band of crystalline limestone, have a general north-east and south-west strike, and are much folded, exhibiting pretty symmetrical anticlinal, and synclinal, in which the strata are seen to dip at various angles, sometimes as low as 25 degrees or 30 degrees, but more often approaching the vertical. The bedded deposits of apatite, which are found running and dipping with these, I am disposed to look upon as true beds, deposited at the same time with the enclosing rocks. The veins, on the contrary, cut across all these strata, and in some noticeable instances include broken angular masses of the enclosing rocks. They are, for the most part, nearly at right angles to the strike of the strata, and generally vertical, though to both of these conditions there are exceptions. One vein, which had yielded many hundred tons of apatite, I found to intersect, in a nearly horizontal attitude, vertical strata of gneiss, and in rare cases what appear from their structure and composition to be veins are found coinciding in dip and in strike with the enclosing strata."

The apatites of Norway are known since 1854, and occur on the southern coast in similar rocks to our own (Canadian), and many of the associated minerals are similar to those observed in the Laurentian rocks, the vein matter differing chiefly in freedom from carbonate of lime.

Rutile may be mentioned as an exception, which in some minds is so abundant as to form a considerable revenue to a working mine, since it is worth 1s. 6d. per lb., say \$800 per ton. These are fluor-apatites, although they contain also some chlorine.

Continental geologists (Brogger and Rensch) who have studied these formations have supposed them to be of eruptive origin, in consequence of the absence of phosphoric acid in the surrounding rocks, but the question seems to be most doubtful, as well here as in the case of the same opinion held on the Canadian apatite deposits.

The Situation of Canadian Phosphate Trade.

Although this Canadian industry has not progressed on the same scale as many other phosphate fields, Somme, Ciply, Liège, Carolina, and Florida, yet there are some facts offering an explanation for this. The peculiarity of the occurrence of the mineral in vein-like formation in hard rock, calls for a scientific and economic system of mining, which has been little applied to the development of our deposits, and the cost of production is thereby more considerable than that attained in other fields of supply.

Certain centres of manure manufacture still require our high testing products to complete their standard types of concentrated supers, and the rapidly increasing demand for fertilisers by all the civilised world, both the new and the old, will tend to maintain a fair value for natural phosphates. We are getting into the era in which steam does not work fast enough, and on every hand we are seeking to accomplish our ends by electricity with lightning speed. Someone has said that the man who could make two blades of grass grow where one grew before was a benefactor to his race, but the rush and the struggle for existence imposes that every cultivator shall be a benefactor in this regard, and carry on agricultural science at the highest possible tension for his very existence.

With increasing populations, with better means of transport, and lastly, but not least, advanced scientific education, fertilisers and all other artificial means of stimulating our exhausted soils will continue to be in increasing demand.

We see no reason, therefore, to suppose that the mineral phosphate industry or phosphate mining has attained its zenith, and so far as we can see at present, the future demands of the world for phosphoric acid are destined to increase with time and agricultural progress.

Résumé.

We may shortly generalise the foregoing facts and observations.

Of the sixty-four elementary substances at present known to compose the material of our original globe, phosphorus is found to be among the twenty more abundant elements, and is recognised to have been widely disseminated in all the original and ancient rock masses. With the exception of the segregations of crystallised apatite in the Laurentian rocks, we do not find any marked local accumulation of phosphatic bases in any of the azoic formations or intrusive rocks.

The existence of the Eozoon Canadense is still debatable, and it is problematical whether the apatite of these older metamorphosed strata is not the mineralised product of organic remains, but passing from the Laurentian epoch to the succeeding and less altered rocks we are immediately in presence of abundant evidence of organised life, and cannot fail to remark how much more frequent are the accumulations of phosphatic beds.

The function of organised life to assimilate and concentrate the disseminated phosphoric element is strikingly apparent. The natural forces which are ever restless and continual in building up the varied geological strata of succeeding epochs (attrition, deposition, cementation, ablation, &c.) may alter and vary the manner of presentation of the phosphatic deposits which we have been considering, but the silently working power of assimilation by the organised cell would appear to triumph over the mighty disruptive and more violent operations of nature, for the latter forces fail to re-disseminate the work accomplished by the former, but rather complete the task required to secure to man the providential supplies of phosphatic deposits with which we may satisfy our pre-

sent demands, and therefore these economic supplies are seen to be chiefly in the more recent geological formations.

A REVISION OF THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 48).

MANY varieties of cupric oxide were examined. Material obtained from the carbonate, or by precipitation from the sulphate, evolved little or no gas, thus affording an admirable proof of the purity of the acid and water. Check experiments with such material were accordingly made from time to time. Other circumstances being equal, the purer the oxide the more gas was evolved. Solid impurities, such as alkaline salts, seemed partially to prevent the occlusion.

The volumes of gas are given without any correction, the temperature and pressure remaining so nearly constant that the observations are not recorded. The following Table is intended only as a basis of rough comparison. The gas was frequently analysed, with results similar to those tabulated above. The results confirm those of the preceding series.

The higher temperatures recorded above are merely approximate guesses. 600° signifies a dull red heat, 700° a medium red heat, and 900° a very bright red heat. In Experiment 92 the oxide was heated at the highest temperature obtainable by a Berzelius spirit lamp. In No. 94 the material was heated for an hour and a half in the Berzelius lamp, and then for an hour in a glass tube under a stream of oxygen. The oxide was transferred while warm to the bulb apparatus. It evolved upon solution 0.088 per cent of gas, one-eighth of which was oxygen. In the ninetieth experiment hydrochloric acid was used for the solution of the oxide.

The two series of determinations, which were perhaps more numerous than necessary, showed the following important facts:—

First, that cupric oxide prepared by the ignition of the oxy-nitrate after Hampe's method contained between four and five times its volume of occluded gas. (Nos. 58, 63 to 67, 84 to 94).

Second, that ignition of the oxide at very bright redness was capable of expelling a portion of this gas. The temperature required was nevertheless considerably above that which Hampe apparently employed. Nos. 59, 81, and 95).

Third, that beyond a certain limit the time of ignition makes no important difference. (Nos. 86 to 91).

Fourth, that the gas was not absorbed from the air on cooling. (Nos. 64, 65, 66, and others).

Fifth, that specimens of cupric oxide prepared in different ways contained very different amounts of gas. It is a curious fact that material which has been heated only to 300° contained less gaseous nitrogen than that which had been ignited at a higher temperature. In this case the nitrogen may still have existed in the combined form. (Nos. 78, 79, 84, 85).

An explanation for the observed phenomena must necessarily be hypothetical, and will not be attempted at present.

In order to find the direct connection between the loss of weight noticed upon heating cupric oxide and the quantity of gas retained by the substance, the following experiment was made:—

Experiment 101.—Cupric oxide which had been heated to constant weight at dull redness was ignited at bright redness in a double platinum crucible.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

Occluded Gas in Cupric Oxide.—Second Series.

No. of experiment.	Nature of cupric oxide.	Weight of CuO. Grms.	Heat and time of ignition.	Volume of gas evolved. C.c.	Per cent of gas in CuO by weight.	Remarks on method.
68	Blank experiment.	—	—	0'00	—	H ₂ SO ₄ +H ₂ O.
69	" "	—	—	0'00	—	"
70	Precipitated.	1'00	Dull red.	0'10	0'011	Bulbs.
71	" "	1'60	"	0'20	0'013	"
72	From carbonate.	1'50	Dull red.	0'07	0'006	Bulbs.
73	" "	2'00	Dull red exposed to air.	0'10	0'006	"
74	{ Crude, of commerce, contained cuprous oxide. }	3'00	Not ignited.	0'70	0'026	Bulbs.
75		8'00	Dull red.	2'00	0'028	Flask.
76		7'00	Not ignited.	2'00	0'032	Another sample.
77	From carbonate.	1'50	Dull red.	0'05	0'003	Flask.
78	{ Six experiments with CuO prepared by action of CuO on Cu(NO ₃) ₂ and sub- sequent ignition of basic nitrate. }	1'70	Very low.	0'34	0'023	Flask.
79		3'20	Dull red, 3 hours.	1'03	0'036	"
80		1'20	Dull red, 7 hours.	0'25 (?)	0'023 (?)	"
81		1'70	Bright red.	0'09	0'006	"
82		2'00	Dull red.	0'26	0'015	Pump not used.
83		2'00	"	0'73	0'041	" "
84	After Hampe's method.	0'39	310°; 2 hours.	0'17	0'050	Bulbs.
85	" " "	1'10	" "	0'30	0'035	"
86	" " "	1'82	600°; 2 hours.	1'35	0'084	Flask.
87	" " "	0'39	700°; ½ hour.	0'30	0'087	Bulbs.
88	" " "	0'50	600°; 1 hour.	0'33	0'077	"
89	" " "	0'60	600°; 4 hours.	0'41	0'079	"
90	" " "	0'61	" "	0'36	0'070	Used HCl.
91	" " "	0'44	" "	0'29	0'079	Bulbs.
92	New preparation.	2'00	700°; ¾ hour.	1'37	0'080	See above.
93	" "	2'98	600°; 2 hours.	2'12	0'082	Flask.
94	" "	0'98	See above.	0'75	0'088	See above.
95	" "	0'50	900°; 1 hour.	0'17	0'039	—
96	{ From carbonate pre- pared from nitrate. }	0'65	600°; 1 hour.	0'09	0'016	—
97		0'50	290°.	0'10	0'023	—
98	{ From carbonate of com- merce. }	1'00	600°; 1 hour.	0'10	0'011	—
99		0'75	" "	0'03	0'004	—
100	Wire form.	1'00	—	0'01±	0'001±	Contained Cu ₂ O.

	Grms.
Weight of platinum crucible	=18'0889
Weight of crucible+CuO, 2½ hours at dull redness	=19'65852
Weight of crucible+CuO, 4 hours more at dull redness	=19'65846
After ignition at very bright redness (20 minutes)	=19'6574
After ignition at very bright redness (50 minutes more)	=19'6571
Total loss of weight	=0'0014

One grm. of this specimen was shown to contain 0'00081 grm. of occluded gas before ignition and 0'00039 grm. afterward (Experiments 86 to 95). In the quantity taken above, this difference corresponds to a loss of weight of nearly 0'0007 grm., or about half of that observed. The remainder of the loss may have been due to a partial reduction of the oxide. (Compare page 21).

Experiment 102.—In order to discover if heating cupric oxide in a vacuum produced any important evolution of nitrogen, six grms. of cupric oxide were dried in a glass tube with the greatest care, exactly after the manner of Hampe, and weighed in the air. One end of the tube was then sealed, the other was attached to a Sprengel

pump, and the whole was heated to about 500° C. for half an hour. Upon sealing and weighing, the loss of weight was found to amount to 4'4 m.grms. The amount of air displaced was found by opening the tube under boiled water, which wholly filled it. The weight of water, reduced to 4°, was 3'48 grms., while the temperature and pressure of the air at the time of weighing the exhausted tube were respectively 24° C. and 754 m.m. Hence the weight of displaced air must have equalled 4'1 m.grms., or only 0'0003 grm. less than the loss of weight actually observed. Therefore the cupric oxide could not have lost more than 0'005 per cent of its weight under the treatment described.* The moist cupric oxide yielded approximately the usual volume of nitrogen upon solution in acids; but no very accurate measurement was made.

(To be continued).

Reproduction of Purely Potassic Nepheline.—André Duboin.—On continuing his researches on the reactions of silica or potassium hydrofluosilicate upon alumina in presence of an excess of melted potassium fluoride, he has succeeded by prolonging the action of the temperature in obtaining purely potassic nepheline, KO,Al₂O₃,2SiO₂.—*Comptes Rendus*, cxv., No. 1.

* In Experiment 50 the temperature of ignition was somewhat higher.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Continued from p. 45).

ELECTIVE METHODS.

PLAN A.—*Directions for the Examination of Syrups which Contain 2 per cent or more of Invert Sugar, Starch Sugar, or Raffinose, as also of Sugars containing Raffinose.**

In the examination of those syrups, which have been handed over to the chemist because they contain 2 per cent or more of invert sugar, the determination of the specific gravity and degree Brix can be made as previously directed. Naturally the direct determination of the specific gravity by means of the picnometer can take the place of this method, but in no case is it allowable to substitute the estimation of total solids, as on the one hand this would cause differences in the coefficient of purity as obtained by the officers and chemists, and on the other hand the determination of total solids in syrups containing invert sugar is much too difficult and takes up too much time to be of any use in every day practice. In calculating the coefficient of purity the method used in the sugar-house, namely, considering only sucrose as sugar, cannot be used, but the invert sugar must be calculated as sucrose by deducting one-twentieth of the amount found, adding to the direct content of sucrose and basing the calculation of this result.

For the determination of the sugar-content various methods can be applied according to the amount of invert sugar, starch sugar, or raffinose present. The following remarks will offer some explanation:—

The invert sugar of syrups is very often inactive, but can nevertheless have the power of rotating to the left, which deviation, according to late investigations, is 0.33, according to others 0.34 times as great as the right-handed rotation of sucrose. Consequently, as soon as considerable invert sugar is present, the polarisation of the sucrose present will be correspondingly diminished. As is well known Meissl proposed in the examination of colonial sugars to multiply the invert sugar found by 0.34, add this to the polarisation, and thus arrive at the correct amount of sucrose. This method would, however, be out of place in the analysis of syrups, as the invert sugar present very often does not show its normal rotatory power, but varies down to complete inactivity. Meissl's correction in such cases would lead to unreliable results. At the same time the rotatory power of the invert sugar may cause the results to be too low. In considering all these circumstances it becomes obvious that the determination of total sugar from the polarisation, and the invert sugar found, is only possible when the invert sugar present does not exceed a certain percentage. For instance, if 6 per cent of invert sugar were present the amount of sucrose could be $6 \times 0.33 = 1.98$ per cent too low. Therefore, as the syrups handed to the chemist for examination may contain considerable quantities of invert sugar whose rotatory power we do not know, we recommend the rejection of the optical method completely, and the adoption of a gravimetric one, a new and easy modification of which will be given under I.

The presence of starch sugar or raffinose makes a difference. The reducing power of starch sugar, which in the commercial article presents a variation corresponding to from 40—60 per cent of sugar, is not changed by the conditions under which the inversion of sugar syrups is made in the gravimetric method; and as we cannot determine the quantity of starch sugar present accurately, the gravimetric method for the estimation of the total content of beet sugar and of the quotient of purity is no longer applicable. It would, on the contrary, lead to

large errors, and syrups having a coefficient of purity of over 70 would, if examined by this method, after the addition of a certain quantity of starch sugar, appear to be below 70. In such cases, where starch sugar is present, the influence exerted by the laevo-rotation of the invert sugar upon the polarisation can no more be considered, as starch sugar has a higher dextro-rotatory power than the other sugars present. To avoid mistakes, which could be easily caused by adding starch sugar to syrups of a coefficient of purity of over 70, it is best, when starch sugar is present, to calculate the real sucrose content from the polarisation and the invert sugar directly determined. This method is described under II. If raffinose is present still another method, which will be found under III. must be adopted.

I.—*The Presence of Starch Sugar need not be considered.*

The examination of syrups which do not contain any starch sugar syrup will be a common occurrence, as such an addition is generally not made by the manufacturers themselves, but rather by the dealers. One operation will here suffice for the determination of total sugar.

Weigh out one-half the normal weight (13.024 grms.) of syrup, dissolve in a 100 c.c. flask in 75 c.c. of water, add 5 c.c. hydrochloric acid (38.8 per cent HCl), and warm in a water-bath to 67—70° C. As soon as the contents of the flask have reached this temperature heat for five minutes, not allowing the temperature to rise above 70° C., and shaking frequently. As the previous warming will take from two and a half to five minutes, the whole operation will require from seven and a half to ten minutes. Fill up to the mark, shake, and dilute 50 c.c. of this solution to a litre. By means of a pipette, transfer 25 c.c. of this to a flask and add 25 c.c. of a solution of sodium carbonate (170 grms. anhydrous salt to the litre) to neutralise

Table for Calculating the Sucrose corresponding to the Invert Sugar Present from the Copper Found on Three Minutes' Boiling.

Sucrose. M.grm.	Copper. M.grm.	Sucrose. M.grm.	Copper. M.grm.	Sucrose. M.grm.	Copper. M.grm.	Sucrose. M.grm.	Copper. M.grm.
40	79.0	73	145.2	105	208.6	139	269.1
41	81.0	74	147.1	107	210.5	140	270.9
42	83.0	75	149.1	108	212.3	141	272.7
43	85.2	76	151.0	109	214.2	142	274.5
44	87.2	77	153.0	110	216.1	143	276.3
45	89.2	78	155.0	111	217.9	144	278.1
46	91.2	79	156.9	112	219.8	145	279.9
47	93.3	80	158.9	113	221.6	146	281.6
48	95.3	81	160.8	114	223.5	147	283.4
49	97.3	82	162.8	115	225.3	148	285.2
50	99.3	83	164.7	116	227.2	149	286.9
51	101.3	84	166.6	117	229.0	150	288.8
52	103.3	85	168.6	118	230.9	151	290.5
53	105.3	86	170.5	119	232.8	152	292.3
54	107.3	87	172.4	120	234.6	153	294.0
55	109.4	88	174.3	121	236.4	154	295.7
56	111.4	89	176.3	122	238.3	155	297.5
57	113.4	90	178.2	123	240.2	156	299.2
58	115.4	91	180.1	124	242.0	157	300.9
59	117.4	92	182.0	125	243.9	158	302.6
60	119.5	93	183.9	126	245.7	159	304.4
61	121.5	94	185.8	127	247.5	160	306.1
62	123.5	95	187.8	128	249.3	161	307.8
63	125.4	96	189.7	129	251.2	162	309.5
64	127.4	97	191.6	130	252.9	163	311.3
65	129.4	98	193.5	131	254.7	164	313.0
66	131.4	99	195.4	132	256.5	165	314.7
67	133.4	100	197.3	133	258.3	166	316.4
68	135.3	101	199.2	134	260.1	167	318.1
69	137.3	102	201.1	135	261.9	168	319.9
70	139.3	103	202.9	136	263.7	169	321.6
71	141.3	104	204.8	137	265.5	170	323.3
72	143.2	105	206.7	138	267.3		

* Official German method used in taxing sugars (*Zeit. Anal. Chem.*, vol. xxviii., No. 2.

the free acid present. Add 50 c.c. of Soxhlet's solution, heat to boiling, as in the determination of invert sugar, and keep the liquid in ebullition for three minutes. As all the sucrose in this solution has been inverted, and is therefore unable to influence the result, we need not be so careful about the time of boiling. Soxhlet's experiments show that two or three minutes difference will not influence the result materially. Dilute the liquid with an equal volume of water, which has been previously boiled so as to expel air, and continue as directed under the determination of invert sugar. The tables so far published for the calculation of results are of no value in this case, as they have been constructed with regard to glucose or a mixture of invert sugar and saccharose. The following table has been compiled for invert sugar, and enables the analyst to calculate the amount of sucrose directly from the amount of copper found.

Example: 25 c.c. of the solution = 0.1628 grm. substance, gave 0.1628 grm. of copper, which corresponds to 0.082 grm. of sugar. Therefore the syrup contained 50.4 per cent sugar.

Supposing that this syrup showed 80° Brix, then its coefficient would be 63. This coefficient is only calculated to tenths, hundredths in the case of the degree Brix being taken as an additional tenth, while with the co-efficient they are not considered, thus 82.85 Brix would be read 82.9, while a coefficient of 69.99 is taken as 69.9, and not 70.

(To be continued.)

THE PROPOSED "HOFMANN HOUSE."

THE German Chemical Society, in seeking to do well-merited honour to their late illustrious president, Prof. August Wilhelm von Hofmann, have struck out a new idea. They are not content with erecting a monument, column, obelisk, or the like at his grave or in some conspicuous place in Berlin. Their project includes, indeed, a splendid statue of the defunct discoverer, but it comprises something much more practical,—something to which the sternest utilitarianism of the old school could not object!

The Hofmann House is to include, in the first place, a locality—and we may presume a fully-equipped locality—for chemical investigations. Numerous and well arranged as are the laboratories of modern Germany, the Berlin Chemical Society conceive that erecting another not specially attached to any of the Universities, and connected with the reminiscences of Hofmann, will be a graceful tribute to the memory of him we have lost and a useful way of continuing his labours.

Another object of the proposed "Hofmann House" is to afford an occasional home for other scientific associations. Hence we presume that lectures, scientific congresses, demonstrations, and exhibitions will find here a welcome.

We need scarcely add that no nobler way of doing posthumous homage to a man like Hofmann could be devised.

We have had in this country men whom we might well have honoured in a similar manner.

The Institute of Chemistry of Great Britain and Ireland.—At the examination in Practical Chemistry for admission to the Institute, held from Monday, 11th, to Friday, 15th July, thirty-seven candidates presented themselves, of whom the following nineteen were successful:—Mr. E. C. Baly, Mr. F. J. Bloomer, Mr. A. C. Chapman, Mr. J. C. Chorley, Mr. F. Dent, Mr. F. E. Francis, Mr. A. F. Fryer, Mr. F. J. Hambly, Mr. E. E. Johnson, Mr. T. Kendrew, Mr. C. Leigh, Miss E. J. Lloyd, Mr. H. H. Mann, Mr. C. H. New, Mr. T. H. Norris, Mr. W. Orr, Mr. N. S. Rudolf, Mr. W. D. Sawers, and Mr. A. E. Wareing.

PROCEEDINGS OF SOCIETIES.

THE SOCIETY OF CHEMICAL INDUSTRY.

THIS Society has just held its Annual General Meeting on the 20th, 21st, and 22nd instant, under the Presidency of Dr. J. EMERSON REYNOLDS, F.R.S. The meeting was very numerous attended; indeed, it is probable that this will always be the case with London meetings. A member, *e.g.*, living in Manchester, if the meeting is not held in his own city, would much rather go to London than to Bristol, Newcastle, or Glasgow.

The meeting of the Council took place on Wednesday, July 20, at 2.30 p.m., in the Hall of the Drapers' Company, Throgmorton St., City, and the General Meeting at 3 p.m.

A reception by the President ensued at 8 p.m. in the galleries of the Royal Institute of Painters in Water-Colours, Piccadilly, W., followed at 8.30 p.m. by a smoking concert.

The second day was devoted to visits to works on the Thames. Two only of the works visited, those of the Union Oil Mills and of the Lindé Ice Works, could, strictly speaking, be called chemical works.

The excursion to Windsor and Cliveden was held on Friday, July 22nd, amidst brilliant weather, and was splendidly successful. The number of members and friends present was estimated at 500. The only drawback on this occasion was a lack of punctuality, due, we must add, not to the Council, to the efficient general secretary, Mr. C. G. Cresswell, or the London honorary secretary, Mr. J. Heron, but to the dilatoriness of some of the members and their friends. The special train for Windsor was timed to leave Paddington Station at 9.50 a.m., reaching the Royal Borough about 10 a.m. In sober sadness the train started only about 10 a.m., those who had already taken their seats having had their ears regaled with the hammering, consequent upon repairs, of the iron roof of the station.

At Windsor the scenery was unusually beautiful owing to the glowing sunshine following upon the rains in the earlier part of the week. The State Apartments, the Terraces, and the Round Tower were duly visited. At 12 noon an organ recital took place in St. George's Chapel. At 1 o'clock ensued luncheon in the Town Hall, the use of which was kindly granted to the Society by the Worshipful the Mayor of Windsor, J. Brown, Esq.

At 2.40 p.m. the party went down to the Quay and embarked in steam launches for Cliveden, the seat of the Duke of Westminster. The hill sides, covered with a rich and varied growth of trees and shrubs, were universally admired. Tea was partaken of in the "Cottage" in the woods, by the kind permission of the Duke of Westminster.

The return voyage was not quite felicitous. On approaching Boulter's Lock it was found that four launches were just in front, whilst a fleet of barges were coming in the opposite direction. "First come first served" is the sensible rule of the Conservators, so the party had to submit to heavy demands upon their patience.

NOTICES OF BOOKS.

Transactions of the Canadian Institute. No. 4. April, 1892. Vol. ii., Part 2.

A GREAT part of the subject-matter of these *Transactions* lies quite outside the boundaries of Science.

Two papers on the "Yellows in Peaches" and on the "Blood of the Amphibia" are, of course, biological. The paper on the "Possibilities of Iron and Steel Production in Ontario" is not so much technical as commercial or economical. The "Contributions to Geology" consist of references to papers in the *Transactions* of the Canadian Institute.

CORRESPONDENCE.

AN OBSTACLE TO SCIENTIFIC PROGRESS.

To the Editor of the Chemical News.

SIR,—Dr. Gore's suggestive remarks upon this subject are framed in the spirit of appreciative criticism, and I venture to follow him with a few reflections which I believe to be similarly animated.

A short time since I happened to take the silent part in a conversation between a well-known M.P. and a distinguished member of the late (as of the next to be) government. The subject was the "latest mistake" of the present government, and upon this the ex-minister delivered himself as follows:—"Having been a member of more than one Cabinet I am always prepared to find sixteen men in conclave deciding upon that which each individual would consider an act of folly."

In this reflection it was not the party man but the philosopher who spoke, and the truism is as general to the scientific as to the political world.

No chemist in this country would call in question for a moment the capabilities or the motives—in respect of the discharge of official duties—of the individuals composing the Councils or Committees who administer the affairs of our learned or professional societies, nor hesitate to concede, *a priori*, that their collective judgment on any matter of the science was considerably more trustworthy than his own. But history, on the other hand, written or unwritten, would not confirm him in an uninquiring trust in the collective wisdom of these bodies *in action*. They are frequently worsted in controversy with individuals in smaller matters, and on broad questions of policy evince an indecision and want of grasp which compel the individual to reason, as the ex-minister above quoted, that a council of able men may be "an ass"—to use with due reservation and apology the classic simile.

Dr. Gore preaches forcibly the essential individualism of scientific work and progress; our learned societies, on the other hand, legislate for average truth and the average man, the non-existent individual born of statistics and convention.

Dr. Gore upholds, between the lines, that where there is no prophet the people perish. The Institute of Chemistry inculcates the lively doctrine that where there are no profits the chemist perishes. We most look to the Chemical Society to look after the prophets and the S.C. must consistently apply trades union principles for the purpose of raising profits. There is not doubt the Chemical Society can do much more than it does towards the encouragement of research; but, more important still, the individual chemist can do much to encourage the Society to encourage original enterprise, by quietly contributing to the breaking down of the "fixed ideas" by which it is generally, and the "conspiracy of silence" by which it is occasionally, dominated. The crusade undertaken by the Institute is of course based upon utilitarianism and expediency, and may be left out of consideration as a progressive movement of the Science *qua* Science. For such progress the world has to look to the individual worker; the individual wants liberty and opportunity, and too often meets with restraints and "mild repression." Dr. Gore has called attention to the existence of such obstacles to progress; he has stated his case temperately, and his statement will be the more likely, therefore, to command attention at head quarters.—I am, &c.,

X.

AN OBSTACLE TO SCIENTIFIC PROGRESS.

To the Editor of the Chemical News.

SIR,—No more important matter of general interest has, I fancy, appeared in your pages for some time than the

article by Dr. Gore, F.R.S., in the CHEMICAL NEWS, vol. lvi., p. 39. Much the same ideas suggested themselves to me on reading Lord Rayleigh's account of Mr. Waterston's paper in *Nature* a few weeks ago. The tendency to fixedness of habitual thought no doubt becomes greater and greater as the individual brain loses its plasticity; and this law perhaps explains why we have so constantly to deprecate the reluctance of seniors in a science to recognise the work of a junior, if it happens not to be "orthodox." I have had occasion, and shall have soon occasion again, to say strong things upon this subject; for the evil is magnified where "the interested influence of a close profession" comes into the court of judgment. The moral of the whole thing is (1) that we want a research department of a purely professorial character, such as we hope to see in the University of London in the future; (2) that the "referee system" which prevails in some of the "learned societies" has broken down, and needs to be superseded by standing "committees of publication," such as are in vogue at the Chemical Society. The responsibility is too much for an individual referee, especially if he is the nominee of the President, and it becomes a matter of course for the council to simply endorse and act upon his judgment.—I am, &c.,

A. IRVING.

Wellington College, July 25, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 1, July 4, 1892.

Contributions to the Study of the Function of Camphoric Acid.—A. Haller.—Not susceptible of useful abstraction.

Composition of Water, and on Gay-Lussac's Law of Volumes.—A. Leduc.—The author finds from his experiments, and from a comparison of the most recent determinations, the atomic weight of oxygen as 15.88, whilst its density with reference to hydrogen is 15.90. This result has a decided importance for the fixation of the atomic weights of the elementary bodies. The values given by Stas, *e.g.*, require to be multiplied by 0.995. The author finds in the comparison of these numbers a very remarkable confirmation of Gay-Lussac's law of volumes. The numbers hitherto admitted do not permit us to deduce the ponderal composition of gaseous compounds from their composition in volumes or reciprocally. Hitherto Gay-Lussac's law could only be regarded as an approximation. From what has been said it appears to be an exact law.

Nitrogenous Salts of Platinum.—M. Vèzes.—The author has previously described several chloronitrogenous, bromonitrogenous, and iodonitrogenous salts of potassium and platinum, of a composition intermediate between potassium platonitrite, $\text{Pt}(\text{NO}_2)_4\text{K}_2$, and the saturated haloid salt PtX_6K_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). He has since obtained several new salts of the same kind, and which, taken along with the former, constitute regular series. These compounds he now describes in their series.

Researches on the Sodium Pyrogallols.—M. de Forcrand.—A thermo-chemical paper not admitting of abstraction, and scarcely of sufficient interest to justify its insertion *in extenso*.

On Acetono-Resorcine.—H. Causse.—From the author's researches it results that acetone combines with resorcine to form an acetal. This compound, crystalline acetono-resorcine, results from the union of 2 mols. of

resorcin with 1 mol. of acetone, with elimination of 1 mol. of water. It contains only two free phenolic functions.

Utilisation of Burnt Pyrites for the Production of Salts of Iron.—A. and P. Buisine.—The authors mix roasted pyrites in fine powder with sulphuric acid at from 50° to 60° B. in sufficient quantity to saturate all the ferric oxide. The most suitable temperature is 300°. The sulphate thus obtained is a grey powder easy of packing and transport. Ferric chloride may be prepared by passing hydrochloric acid gas into a column filled with roasted pyrites. These ferric salts may be used in agriculture, in the purification of coal-gas, as a mordant in dyeing, as a precipitant for sewage, &c.

The Alterations of Chalybeate Waters.—F. Parmentier.—The author calls in question some of the results recently brought forward by M. Riban. He doubts the authenticity of M. Riban's samples, which were obtained at a "pharmacy." He does not consider the permanganate process suitable for the determination of iron under such circumstances.

On the Passage of Dissolved Substances through Mineral Filters and Capillary Tubes.—C. Chabré.—The most important question is to know what happens if albuminous solutions are passed not through porous earth but simply through a very fine capillary tube. We observe first the passage of a solution less rich in albumen than the original solution, which becomes by degrees proportionally richer; then the passage of the solution thus concentrated is retarded, or perhaps a total stoppage of the flow if the percentage of albumen becomes too large.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 10.

Certain Properties of Manganese.—The chemical reactions of manganese as left by distillation from its amalgam have not been much studied. The metal thus obtained is pyrophoric, and decomposes certain of the most stable substances. In a current of carbon monoxide it burns with heat sufficient to raise the metal to white redness, and the decomposition of the gas is so rapid as to produce a partial vacuum in the apparatus. The action of carbon dioxide upon pyrophoric manganese is the same as that of carbon monoxide. Pyrophoric manganese reacts also upon gaseous sulphurous acid. With nitrogen dioxide and boron chloride there is also rapid absorption and great liberation of heat.

Action of Carbon Monoxide upon Iron.—M. Guntz, —Stammer, Deville, Lowthian Bell, and Schutzenberger observe that carbon monoxide is decomposed by iron, with deposition of carbon. Carbon monoxide, though very stable at high temperatures, is easily decomposed under the influence of oxidisable substances. If we take a pyrophoric iron obtained by igniting the oxalate, the action of carbon monoxide is the same, but less intense, as the metal has been reduced at a higher temperature. This reaction explains why in a certain zone of the blast furnace spongy iron meeting carbon monoxide is oxidised, yielding carbon and ferrous oxide, whilst in another zone this oxide is reduced by the carbon monoxide to yield iron and carbon dioxide, whilst finally, in passing into the hot zones of the furnace, the iron in contact with finely divided carbon is easily oxidised.

Analysis of Certain English Cheeses.—Dr. A. B. Griffiths.—Analyses of Stilton, Cheddar, Gloucester, Leicester, Cheshire, Cotherstone, Dorset, and Wiltshire cheeses. The two latter are poorest in fatty matter.

The Constitution of Milk.—L. Vaudin.—The author points out the very low degree of acidity in the milk of non-ruminant animals, which has hence been considered neutral or even alkaline. The milk of the ruminants is comparatively rich in acid and fluctuates little.

Amidonaphtholsulphonic Acids.—F. Reverdin and Ch. de la Harpe.—This lengthy memoir does not admit of useful abridgment.

Action of Acids upon Blood, and Formation of Oxyhæmoglobine by means of Hæmatine and Albumenoid Matter.—M. Bertin-Sans and J. Moitessier.—The authors have split up oxyhæmoglobine into hæmatine and albumenoid substance, and are now seeking to obtain synthetic hæmoglobine.

Transformation of Cupreine into Quinine and Homologous Bases.—E. Grimaux and E. Arnaud.—This paper also is not adapted for useful abridgment.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 76.

The Deacon Process.—J. Kolb.—An elaborate discussion of the Deacon process in comparison with its rivals, especially the Weldon process. He considers that the Deacon process "has not said its last word." Its installation for an equal production is not appreciably more costly than the Weldon, and it requires less outlay for maintenance, for labour, and for fuel. The objection raised against it of yielding poor gases is not well founded. For anyone who has thoroughly studied the conditions of moisture and of temperature most favourable to the reaction, the problem of making a very rich chloride of lime with gases not containing more than 2 per cent of chlorine presents little difficulty. The future of the Deacon process is involved in that of the Leblanc process, and in the demand for sodium sulphate in the glass manufacture.

The Rodger Process for Melting Antimony.—From the *Journal of the Society of Chemical Industry.*

MISCELLANEOUS.

A Treatise on Manures.—Messrs. Whittaker and Co. have just issued a new edition of Dr. A. B. Griffiths's "Treatise on Manures." The present edition has been enlarged by fifty pages of new matter.

Specific Gravity of Silks.—Leo Vignon.—Already noticed. (We may mention it as an unfortunate circumstance that in France one and the same paper may be sent to two journals or be read before two societies without anything to show that each is not a distinct and independent document. This practice occasions waste of time and trouble to persons who wish to collate the literature of the subject.—*Bull. de la Soc. Chim. de Paris*, vii., No. 9.)

Apparatus for Determining the Temperature of Explosions.—S. Bein (*Zeit. Angew. Chemie*).—A double cylinder of sheet-iron supports in its conical neck an inserted test-tube containing a little sand. The test-tube is closed with a cork having two perforations through which pass a thermometer and a tube-funnel. When the temperature is near the explosion point, small portions of the substance in question are dropped in through the tube-funnel and explode on continued heating. The temperature is read off on the thermometer.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Acid for Etching Copper.—Will you kindly inform me what acids can be used for biting copper in the form of a paste, and which could be worked on with a camel hair or sable brush.—T. BEECH.

THE CHEMICAL NEWS.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

EDINBURGH, 1892.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR ARCHIBALD GEIKIE, LL.D., D.Sc.,
For. Sec. R.S., F.R.S.E., F.G.S., Director-General of
the Geological Survey of the United Kingdom.

In its beneficent progress through these islands the British Association for the Advancement of Science now for the fourth time receives a welcome in this ancient capital. Once again, under the shadow of these antique towers, crowded memories of a romantic past fill our thoughts. The stormy annals of Scotland seem to move in procession before our eyes as we walk these streets, whose names and traditions have been made familiar to the civilised world by the genius of literature. At every turn, too, we are reminded, by the monuments which a grateful city has erected, that for many generations the pursuits which we are now assembled to foster have had their congenial home. Literature, philosophy, science, have each in turn been guided by the influence of the great masters who have lived here, and whose renown is the brightest gem in the chaplet around the brow of this "Queen of the North."

Lingering for a moment over these local associations, we shall find a peculiar appropriateness in the time of this renewed visit of the Association to Edinburgh. A hundred years ago a remarkable group of men was discussing here the great problem of the history of the earth. James Hutton, after many years of travel and reflection, had communicated to the Royal Society of this city, in the year 1785, the first outlines of his famous "Theory of the Earth." Among those with whom he took counsel in the elaboration of his doctrines were Black, the illustrious discoverer of "fixed air" and "latent heat"; Clerk, the sagacious inventor of the system of breaking the enemy's line in naval tactics; Hall, whose fertile ingenuity devised the first system of experiments in illustration of the structure and origin of rocks; and Playfair, through whose sympathetic enthusiasm and literary skill Hutton's views came ultimately to be understood and appreciated by the world at large. With these friends, so well able to comprehend and criticise his efforts to pierce the veil that shrouded the history of this globe, he paced the streets amid which we are now gathered together; with them he sought the crags and ravines around us, wherein Nature has laid open so many impressive records of her past; with them he sallied forth on those memorable expeditions to distant parts of Scotland, whence he returned laden with treasures from a field of observation which, though now so familiar, was then almost untrodden. The centenary of Hutton's "Theory of the Earth" is an event in the annals of science which seems most fittingly celebrated by a meeting of the British Association in Edinburgh.

In choosing from among the many subjects which might properly engage your attention on the present occasion, I have thought that it would not be inappropriate nor uninteresting to consider the more salient features of that "Theory," and to mark how much in certain departments of inquiry has sprung from the fruitful teaching of its author and his associates.

It was a fundamental doctrine of Hutton and his school that this globe has not always worn the aspect which it bears at present; that, on the contrary, proofs may everywhere be culled that the land which we now see has been formed out of the wreck of an older land. Among these proofs, the most obvious are supplied by some of the more familiar kinds of rock, which teach us that, though they are now portions of the dry land, they were originally sheets of gravel, sand, and mud, which had been worn from the face of long-vanished continents, and after being spread out over the floor of the sea were consolidated into compact stone, and were finally broken up and raised once more to form part of the dry land. This cycle of change involved two great systems of natural processes. On the one hand, men were taught that by the action of running water the materials of the solid land are in a state of continual decay and transport to the ocean. On the other hand, the ocean-floor is liable from time to time to be upheaved by some stupendous internal force akin to that which gives rise to the volcano and the earthquake. Hutton further perceived that not only had the consolidated materials been disrupted and elevated, but that masses of molten rock had been thrust upward among them, and had cooled and crystallised in large bodies of granite and other eruptive rocks which form so prominent a feature on the earth's surface.

It was a special characteristic of this philosophical system that it sought in the changes now in progress on the earth's surface an explanation of those which occurred in older times. Its founder refused to invent causes or modes of operation, for those with which he was familiar seemed to him adequate to solve the problems with which he attempted to deal. Nowhere was the profoundness of his insight more astonishing than in the clear, definite way in which he proclaimed and reiterated his doctrine, that every part of the surface of the continents, from mountain-top to sea-shore, is continually undergoing decay, and is thus slowly travelling to the sea. He saw that no sooner will the sea-floor be elevated into new land than it must necessarily become a prey to this universal and unceasing degradation. He perceived that, as the transport of disintegrated material is carried on chiefly by running water, rivers must slowly dig out for themselves the channels in which they flow, and thus that a system of valleys, radiating from the water-parting of a country, must necessarily result from the descent of the streams from the mountain-crests to the sea. He discerned that this ceaseless and widespread decay would eventually lead to the entire demolition of the dry land, but he contended that from time to time this catastrophe is prevented by the operation of the underground forces, whereby new continents are upheaved from the bed of the ocean. And thus in his system a due proportion is maintained between land and water, and the condition of the earth as a habitable globe is preserved.

A theory of the earth so simple in outline, so bold in conception, so full of suggestion, and resting on so broad a base of observation and reflection, ought, we might think, to have commanded at once the attention of men of science, even if it did not immediately awaken the interest of the outside world; but, as Playfair sorrowfully admitted, it attracted notice only very slowly, and several years elapsed before anyone showed himself publicly concerned about it, either as an enemy or a friend. Some of its earliest critics assailed it for what they asserted to be its irreligious tendency—an accusation which Hutton repudiated with much warmth. The sneer levelled by Cowper a few years earlier at all inquiries into the history of the universe was perfectly natural and intelligible from that poet's point of view. There was then a widespread belief that this world came into existence some six thousand years ago, and that any attempt greatly to increase that antiquity was meant as a blow to the authority of Holy Writ. So far, however, from aiming at the overthrow of orthodox beliefs, Hutton evidently regarded his "Theory" as an important con-

tribution in aid of natural religion. He dwelt with unfeigned pleasure on the multitude of proofs which he was able to accumulate of an orderly design in the operations of Nature, decay and renovation being so nicely balanced as to maintain the habitable condition of the planet. But as he refused to admit the predominance of violent action in terrestrial changes, and on the contrary contended for the efficacy of the quiet, continuous processes which we can even now see at work around us, he was constrained to require an unlimited duration of past time for the production of those revolutions of which he perceived such clear and abundant proofs in the crust of the earth. The general public, however, failed to comprehend that the doctrine of the high antiquity of the globe was not inconsistent with the comparatively recent appearance of man—a distinction which seems so obvious now.

Hutton died in 1797, beloved and regretted by the circle of friends who had learned to appreciate his estimable character and to admire his genius, but with little recognition from the world at large. Men knew not then that a great master had passed away from their midst, who had laid broad and deep the foundations of a new science; that his name would become a household word in after generations, and that pilgrims would come from distant lands to visit the scenes from which he drew his inspiration.

Many years might have elapsed before Hutton's teaching met with wide acceptance, had its recognition depended solely on his writings of the philosopher himself. For, despite his firm grasp of general principles and his mastery of the minutest details, he had acquired a literary style which, it must be admitted, was singularly unattractive. Fortunately for his fame, as well as for the cause of science, his devoted friend and disciple, Playfair, at once set himself to draw up an exposition of Hutton's views. After five years of labour on this task there appeared the classic "*Illustrations of the Huttonian Theory*," a work which for luminous treatment and graceful diction stands still without a rival in English geological literature. Though professing merely to set forth his friend's doctrines, Playfair's treatise was in many respects an original contribution to science of the highest value. It placed for the first time in the clearest light the whole philosophy of Hutton regarding the history of the earth, and enforced it with a wealth of reasoning and copiousness of illustration which obtained for it a wide appreciation. From long converse with Hutton, and from profound reflection himself, Playfair gained such a comprehension of the whole subject that, discarding the non-essential parts of his master's teaching, he was able to give so lucid and accurate an exposition of the general scheme of Nature's operations on the surface of the globe, that with only slight corrections and expansions his treatise may serve as a text-book to-day. In some respects, indeed, his volume was long in advance of its time. Only, for example, within the present generation has the truth of his teaching in regard to the origin of valleys been generally admitted.

Various causes contributed to retard the progress of the Huttonian doctrines. Especially potent was the influence of the teaching of Werner, who, though he perceived that a definite order of sequence could be recognised among the materials of the earth's crust, had formed singularly narrow conceptions of the great processes whereby that crust has been built up. His enthusiasm, however, fired his disciples with the zeal of proselytes, and they spread themselves over Europe to preach everywhere the artificial system which they had learnt in Saxony. By a curious fate Edinburgh became one of the great headquarters of Wernerism. The friends and followers of Hutton found themselves attacked in their own city by zealots who, proud of superior mineralogical acquirements, turned their most cherished ideas upside down, and assailed them in the uncouth jargon of Freiberg. Inasmuch as subterranean heat had

been invoked by Hutton as a force largely instrumental in consolidating and upheaving the ancient sediments that now form so great a part of the dry land, his followers were nicknamed Plutonists. On the other hand, as the agency of water was almost alone admitted by Werner, who believed the rocks of the earth's crust to have been chiefly chemical precipitates from a primeval universal ocean, those who adopted his views received the equally descriptive name of Neptunists. The battle of these two contending schools raged fiercely here for some years, and though mainly from the youth, zeal, and energy of Jameson, and the influence which his position as Professor in the University gave him, the Wernerian doctrines continued to hold their place, they were eventually abandoned even by Jameson himself, and the debt due to the memory of Hutton and Playfair was tardily acknowledged.

The pursuits and the quarrels of philosophers have from early times been a favourite subject of merriment to the outside world. Such a feud as that between the Plutonists and Neptunists would be sure to furnish abundant matter for the gratification of this propensity. Turning over the pages of Kay's "*Portraits*," where so much that was distinctive of Edinburgh society a hundred years ago is embalmed, we find Hutton's personal peculiarities and pursuits touched off in good-humoured caricature. In one plate he stands with arms folded and hammer in hand, meditating on the face of a cliff, from which rocky prominences in shape of human faces—perhaps grotesque likenesses of his scientific opponents—grin at him. In another engraving he sits in conclave with his friend Black, possibly arranging for that famous banquet of garden-snails which the two worthies had persuaded themselves to look upon as a strangely neglected form of human food. More than a generation later, when the Huttonists and Wernerists were at the height of their antagonism, the humorous side of the controversy did not escape the notice of the author of "*Waverley*," who, you will remember, when he makes Meg Dods recount the various kinds of wise folk brought by Lady Penelope Pennfeather from Edinburgh to St. Ronan's Well, does not forget to include those who "rin uphill and down dale, knapping the chucky-stanes to pieces wi' hammers, like sae many road-makers run daft, to see how the world was made."

Among the names of the friends and followers of Hutton there is one which on this occasion deserves to be held in especial honour, that of Sir James Hall, of Dunglass. Having accompanied Hutton in some of his excursions, and having discussed with him the problems presented by the rocks of Scotland, Hall was familiar with the views of his master, and was able to supply him with fresh illustrations of them from different parts of the country. Gifted with remarkable originality and ingenuity, he soon perceived that some of the questions involved in the theory of the earth could probably be solved by direct physical experiment. Hutton, however, mistrusted any attempt "to judge of the great operations of Nature by merely kindling a fire and looking into the bottom of a little crucible." Out of deference to this prejudice Hall delayed to carry out his intention during Hutton's lifetime. But afterwards he instituted a remarkable series of researches which are memorable in the history of science as the first methodical endeavour to test the value of geological speculation by an appeal to actual experiment. The Neptunists, in ridiculing the Huttonian doctrine that basalt and similar rocks had once been molten, asserted that, had such been their origin, these masses would now be found in the condition of glass or slag. Hall, however, triumphantly vindicated his friend's view by proving that basalt could be fused, and thereafter by slow cooling could be made to resume a stony texture. Again, Hutton had asserted that under the vast pressures which must be effective deep within the earth's crust, chemical reactions must be powerfully influenced, and that under such conditions even limestone

may conceivably be melted without losing its carbonic acid. Various specious arguments had been adduced against this proposition, but by an ingeniously devised series of experiments Hall succeeded in converting limestone under great pressure into a kind of marble, and even fused it, and found that it then acted vigorously on other rocks. These admirable researches, which laid the foundations of experimental geology, constitute not the least memorable of the services rendered by the Huttonian school to the progress of science.

Clear as was the insight and sagacious the inferences of these great masters in regard to the history of the globe, their vision was necessarily limited by the comparatively narrow range of ascertained fact which up to their time had been established. They taught men to recognise that the present world is built of the ruins of an earlier one, and they explained with admirable perspicacity the operation of the processes whereby the degradation and renovation of land are brought about. But they never dreamed that a long and orderly series of such successive destructions and renewals had taken place, and had left their records in the crust of the earth. They never imagined that from these records it would be possible to establish a determinate chronology that could be read everywhere, and applied to the elucidation of the remotest quarter of the globe. It was by the memorable observations and generalisations of William Smith that this vast extension of our knowledge of the past history of the earth became possible. While the Scottish philosophers were building up their theory here, Smith was quietly ascertaining by extended journeys that the stratified rocks of the West of England occur in a definite sequence, and that each well-marked group of them can be discriminated from the others and identified across the country by means of its enclosed organic remains. It is nearly a hundred years since he made known his views, so that by a curious coincidence we may fitly celebrate on this occasion the centenary of William Smith as well as that of James Hutton. No single discovery has ever had a more momentous and far-reaching influence on the progress of a science than that law of organic succession which Smith established. At first it served merely to determine the order of the stratified rocks of England. But it soon proved to possess a world-wide value, for it was found to furnish the key to the structure of the whole stratified crust of the earth. It showed that within that crust lie the chronicles of a long history of plant and animal life upon this planet, it supplied the means of arranging the materials for this history in true chronological sequence, and it thus opened out a magnificent vista through a vast series of ages, each marked by its own distinctive types of organic life, which, in proportion to their antiquity, departed more and more from the aspect of the living world.

Thus a hundred years ago, by the brilliant theory of Hutton and the fruitful generalisation of Smith, the study of the earth received in our country the impetus which has given birth to the modern science of geology.

To review the marvellous progress which this science has made during the first century of its existence would require not one but many hours for adequate treatment. The march of discovery has advanced along a multitude of different paths, and the domains of Nature which have been included within the growing territories of human knowledge have been many and ample. Nevertheless, there are certain departments of investigation to which we may profitably restrict our attention on the present occasion, and wherein we may see how the leading principles that were proclaimed in this city a hundred years ago have germinated and borne fruit all over the world.

From the earliest times the natural features of the earth's surface have arrested the attention of mankind. The rugged mountain, the cleft ravine, the scarped cliff, the solitary boulder, have stimulated curiosity and prompted many a speculation as to their origin. The shells embedded by millions in the solid rocks of hills

far removed from the sea have still further pressed home these "obstinate questionings." But for many long centuries the advance of inquiry into such matters was arrested by the paramount influence of orthodox theology. It was not merely that the Church opposed itself to the simple and obvious interpretation of these natural phenomena. So implicit had faith become in the accepted views of the earth's age and of the history of creation, that even laymen of intelligence and learning set themselves unbidden and in perfect good faith to explain away the difficulties which Nature so persistently raised up, and to reconcile her teachings with those of the theologians. In the various theories thus originating, the amount of knowledge of natural law usually stood in inverse ratio to the share played in them by an uncontrolled imagination. The speculations, for example, of Burnet, Whiston, Whitehurst, and others in this country, cannot be read now without a smile. In no sense were they scientific researches; they can only be looked upon as exertions of learned ignorance. Springing mainly out of a laudable desire to promote what was believed to be the cause of true religion, they helped to retard inquiry, and exercised in that respect a baneful influence on intellectual progress.

It is the special glory of the Edinburgh school of geology to have cast aside all this fanciful trifling. Hutton boldly proclaimed that it was no part of his philosophy to account for the beginning of things. His concern lay only with the evidence furnished by the earth itself as to its origin. With the intuition of true genius he early perceived that the only solid basis from which to explore what has taken place in bygone time is a knowledge of what is taking place to-day. He thus founded his system upon a careful study of the processes whereby geological changes are now brought about. He felt assured that Nature must be consistent and uniform in her working, and that only in proportion as her operations at the present time are watched and understood will the ancient history of the earth become intelligible. Thus, in his hands, the investigation of the present became the key to the interpretation of the past. The establishment of this great truth was the first step towards the inauguration of a true science of the earth. The doctrine of the uniformity of causation in Nature became the fruitful principle on which the structure of modern geology could be built up.

Fresh life was now breathed into the study of the earth. A new spirit seemed to animate the advance along every pathway of inquiry. Facts that had long been familiar came to possess a wider and deeper meaning when their connection with each other was recognised as parts of one great harmonious system of continuous change. In no department of Nature, for example, was this broader vision more remarkably displayed than in that wherein the circulation of water between land and sea plays the most conspicuous part. From the earliest times men had watched the coming of clouds, the fall of rain, the flow of rivers, and had recognised that on this nicely adjusted machinery the beauty and fertility of the land depend. But they now learnt that this beauty and fertility involve a continual decay of the terrestrial surface; that the soil is a measure of this decay, and would cease to afford us maintenance were it not continually removed and renewed; that through the ceaseless transport of soil by rivers to the sea the face of the land is slowly lowered in level and carved into mountain and valley, and that the materials thus borne outwards to the floor of the ocean are not lost, but accumulate there to form rocks, which in the end will be upraised into new lands. Decay and renovation, in well-balanced proportions, were thus shown to be the system on which the existence of the earth as a habitable globe had been established. It was impossible to conceive that the economy of the planet could be maintained on any other basis. Without the circulation of water the life of plants and animals would be impossible, and with that circula-

tion the decay of the surface of the land and the renovation of its disintegrated materials are necessarily involved.

As it is now so must it have been in past time. Hutton and Playfair pointed to the stratified rocks of the earth's crust as demonstrations that the same processes which are at work to-day have been in operation from a remote antiquity. By thus placing their theory on a basis of actual observation, and providing in the study of existing operations a guide to the interpretation of those in past times, they rescued the investigation of the history of the earth from the speculations of theologians and cosmologists, and established a place for it among the recognised inductive sciences. To the guiding influence of their philosophical system the prodigious strides made by modern geology are in large measure to be attributed. And here in their own city, after the lapse of a hundred years, let us offer to their memory the grateful homage of all who have profited by their labours.

But while we recognise with admiration the far reaching influence of the doctrine of uniformity of causation in the investigation of the history of the earth, we must upon reflection admit that the doctrine has been pushed to an extreme perhaps not contemplated by its original founders. To take the existing conditions of Nature as a platform of actual knowledge from which to start in an inquiry into former conditions was logical and prudent. Obviously, however, human experience, in the few centuries during which attention has been turned to such subjects, has been too brief to warrant any dogmatic assumption that the various natural processes must have been carried on in the past with the same energy, and at the same rate as they are carried on now. Variations in energy might have been legitimately conceded as possible, though not to be allowed without reasonable proof in their favour. It was right to refuse to admit the operation of speculative causes of change when the phenomena were capable of natural and adequate explanation by reference to causes that can be watched and investigated. But it was an error to take for granted that no other kind of process or influence, nor any variation in the rate of activity save those of which man has had actual cognisance, has played a part in the terrestrial economy. The uniformitarian writers laid themselves open to the charge of maintaining a kind of perpetual motion in the machinery of Nature. They could find in the records of the earth's history no evidence of a beginning, no prospect of an end. They saw that many successive renovations and destructions had been effected on the earth's surface, and that this long line of vicissitudes formed a series of which the earliest were lost in antiquity, while the latest were still in progress towards an apparently illimitable future.

The discoveries of William Smith, had they been adequately understood, would have been seen to offer a corrective to this rigidly uniformitarian conception, for they revealed that the crust of the earth contains the long record of an unmistakable order of progression in organic types. They proved that plants and animals have varied widely in successive periods of the earth's history, the present condition of organic life being only the latest phase of a long preceding series, each stage of which recedes further from the existing aspect of things as we trace it backward into the past. And though no relic had yet been found, or indeed was ever likely to be found, of the first living things that appeared upon the earth's surface, the manifest simplification of types in the older formations pointed irresistibly to some beginning from which the long procession had taken its start. If then it could thus be demonstrated that there had been upon the globe an orderly march of living forms from the lowliest grades in early times to man himself to-day, and thus that in one department of her domain, extending through the greater portion of the records of the earth's history, Nature had not been uniform but had followed a vast and noble plan of evolution, surely it might have

been expected that those who discovered and made known this plan would seek to ascertain whether some analogous physical progression from a definite beginning might not be discernible in the framework of the globe itself.

But the early masters of the science laboured under two great disadvantages. In the first place, they found the oldest records of the earth's history so broken up and effaced as to be no longer legible. And in the second place, they lived under the spell of that strong reaction against speculation which followed the bitter controversy between the Neptunists and Plutonists in the earlier decades of the century. They considered themselves bound to search for facts, not to build up theories; and as in the crust of the earth they could find no facts which threw any light upon the primeval constitution and subsequent development of our planet, they shut their ears to any theoretical interpretations that might be offered from other departments of science. It was enough for them to maintain, as Hutton had done, that in the visible structure of the earth itself, no trace can be found of the beginning of things, and that the oldest terrestrial records reveal no physical conditions essentially different from those in which we still live. They doubtless listened with interest to the speculations of Kant, Laplace, and Herschel, on the probable evolution of nebulae, suns, and planets, but it was with the languid interest attaching to ideas that lay outside of their own domain of research. They recognised no practical connection between such speculations and the data furnished by the earth itself as to its own history and progress.

This curious lethargy with respect to theory on the part of men who were popularly regarded as among the most speculative followers of science would probably not have been speedily dispelled by any discovery made within their own field of observation. Even now, after many years of the most diligent research, the first chapters of our planet's history remain undiscovered or undecipherable. On the great terrestrial palimpsest, the earliest inscriptions seem to have been hopelessly effaced by those of later ages. But the question of the primeval condition and subsequent history of the planet might be considered from the side of astronomy and physics. And it was by investigations of this nature that the geological torpor was eventually dissipated. To our illustrious former president, Lord Kelvin, who occupied this chair when the Association last met in Edinburgh, is mainly due the rousing of attention to this subject. By the most convincing arguments he showed how impossible it was to believe in the extreme doctrine of uniformitarianism. And though, owing to uncertainty in regard to some of the data, wide limits of time were postulated by him, he insisted that within these limits the whole evolution of the earth and its inhabitants must have been comprised. While, therefore, the geological doctrine that the present order of Nature must be our guide to the interpretation of the past remained as true and fruitful as ever, it had now to be widened by the reception of evidence furnished by a study of the earth as a planetary body. The secular loss of heat, which demonstrably takes place both from the earth and the sun, made it quite certain that the present could not have been the original condition of the system. This diminution of temperature with all its consequences is not a mere matter of speculation, but a physical fact of the present time as much as any of the familiar physical agencies that affect the surface of the globe. It points with unmistakable directness to that beginning of things of which Hutton and his followers could find no sign.

Another modification or enlargement of the uniformitarian doctrine was brought about by continued investigation of the terrestrial crust and consequent increase of knowledge respecting the history of the earth. Though Hutton and Playfair believed in periodical catastrophes, and indeed required these to recur in order to renew and preserve the habitable condition of our planet, their

successors gradually came to view with repugnance any appeal to abnormal, and especially to violent manifestations of terrestrial vigour, and even persuaded themselves that such slow and comparatively feeble action as had been witnessed by man could alone be recognised in the evidence from which geological history must be compiled. Well do I remember in my own boyhood what a cardinal article of faith this prepossession had become. We were taught by our great and honoured master, Lyell, to believe implicitly in gentle and uniform operations, extended over indefinite periods of time, though possibly some, with the zeal of partisans, carried this belief to an extreme which Lyell himself did not approve. The most stupendous marks of terrestrial disturbance, such as the structure of great mountain chains, were deemed to be more satisfactorily accounted for by slow movements prolonged through indefinite ages than by any sudden convulsion.

What the more extreme members of the uniformitarian school failed to perceive was the absence of all evidence that terrestrial catastrophes, even on a colossal scale, might not be a part of the present economy of this globe. Such occurrences might never seriously affect the whole earth at one time, and might return at such wide intervals that no example of them has yet been chronicled by man. But that they have occurred again and again, and even within comparatively recent geological times, hardly admits of serious doubt. How far at different epochs and in various degrees they may have included the operation of cosmical influences lying wholly outside the planet, and how far they have resulted from movements within the body of the planet itself, must remain for further inquiry. Yet the admission that they have played a part in geological history may be freely made without impairing the real value of the Huttonian doctrine, that in the interpretation of this history our main guide must be a knowledge of the existing processes of terrestrial change.

As the most recent and best known of these great transformations, the Ice Age stands out conspicuously before us. If any one sixty years ago had ventured to affirm that at no very distant date the snows and glaciers of the Arctic regions stretched southwards into France, he would have been treated as a mere visionary theorist. Many of the facts to which he would have appealed in support of his statement were already well known, but they had received various other interpretations. By some observers, notably by Hutton's friend, Sir James Hall, they were believed to be due to violent debacles of water that swept over the face of the land. By others they were attributed to the strong tides and currents of the sea when the land stood at a lower level. The uniformitarian school of Lyell had no difficulty in elevating or depressing land to any required extent. Indeed, when we consider how averse these philosophers were to admit any kind or degree of natural operation other than those of which there was some human experience, we may well wonder at the boldness with which, on sometimes the slenderest evidence, they made land and sea change places, on the one hand submerging mountain ranges, and on the other placing great barriers of land where a deep ocean rolls. They took such liberties with geography because only well-established processes of change were invoked in the operations. Knowing that during the passage of an earthquake a territory bordering the sea may be upraised or sunk a few feet, they drew the sweeping inference that any amount of upheaval or depression of any part of the earth's surface might be claimed in explanation of geological problems. The progress of inquiry, while it has somewhat curtailed this geographical license, has now made known in great detail the strange story of the Ice Age.

There cannot be any doubt that after man had become a denizen of the earth, a great physical change came over the northern hemisphere. The climate, which had previously been so mild that evergreen trees flourished within ten or twelve degrees of the north pole, now be-

came so severe that vast sheets of snow and ice covered the north of Europe and crept southward beyond the south coast of Ireland, almost as far as the southern shores of England, and across the Baltic into France and Germany. This Arctic transformation was not an episode that lasted merely a few seasons, and left the land to resume thereafter its ancient aspect. With various successive fluctuations it must have endured for many thousands of years. When it began to disappear it probably faded away as slowly and imperceptibly as it had advanced, and when it finally vanished it left Europe and North America profoundly changed in the character alike of their scenery and of their inhabitants. The rugged rocky contours of earlier times were ground smooth and polished by the march of the ice across them, while the lower grounds were buried under wide and thick sheets of clay, gravel, and sand, left behind by the melting ice. The varied and abundant flora which had spread so far within the Arctic circle was driven away into more southern and less ungenial climes. But most memorable of all was the extirpation of the prominent large animals which, before the advent of the ice, had roamed over Europe. The lions, hyenas, wild horses, hippopotami, and other creatures either became entirely extinct or were driven into the Mediterranean basin and into Africa. In their place came northern forms—the reindeer, glutton, musk ox, woolly rhinoceros, and mammoth.

Such a marvellous transformation in climate, in scenery, in vegetation and in inhabitants, within what was after all but a brief portion of geological time, though it may have involved no sudden or violent convulsion, is surely entitled to rank as a catastrophe in the history of the globe. It was probably brought about mainly, if not entirely, by the operation of forces external to the earth. No similar calamity having befallen the continents within the time during which man has been recording his experience, the Ice Age might be cited as a contradiction to the doctrine of uniformity. And yet it manifestly arrived as part of the established order of Nature. Whether or not we grant that other ice ages preceded the last great one, we must admit that the conditions under which it arose, so far as we know them, might conceivably have occurred before and may occur again. The various agencies called into play by the extensive refrigeration of the northern hemisphere were not different from those with which we are familiar. Snow fell and glaciers crept as they do to-day. Ice scored and polished rocks exactly as it still does among the Alps and in Norway. There was nothing abnormal in the phenomena save the scale on which they were manifested. And thus, taking a broad view of the whole subject, we recognise the catastrophe, while at the same time we see in its progress the operation of those same natural processes which we know to be integral parts of the machinery whereby the surface of the earth is continually transformed.

Among the debts which science owes to the Huttonian school, not the least memorable is the promulgation of the first well-founded conceptions of the high antiquity of the globe. Some six thousand years had previously been believed to comprise the whole life of the planet, and indeed of the entire universe. When the curtain was then first raised that had veiled the history of the earth, and men, looking beyond the brief span within which they had supposed that history to have been transacted, beheld the records of a long vista of ages stretching far away into a dim illimitable past, the prospect vividly impressed their imagination. Astronomy had made known the immeasurable fields of space; the new science of geology seemed now to reveal boundless distances of time. The more the terrestrial chronicles were studied the farther could the eye range into an antiquity so vast as to defy all attempts to measure or define it. The progress of research continually furnished additional evidence of the enormous duration of the ages that preceded the coming of man, while, as knowledge

increased, periods that were thought to have followed each other consecutively were found to have been separated by prolonged intervals of time. Thus the idea arose and gained universal acceptance that, just as no boundary could be set to the astronomer in his free range through space, so the whole of bygone eternity lay open to the requirements of the geologist. Playfair, re-echoing and expanding Hutton's language, had declared that neither among the records of the earth nor in the planetary motions can any trace be discovered of the beginning or of the end of the present order of things; that no symptom of infancy or of old age has been allowed to appear on the face of Nature, nor any sign by which either the past or the future duration of the universe can be estimated; and that although the Creator may put an end, as He no doubt gave a beginning, to the present system, such a catastrophe will not be brought about by any of the laws now existing, and is not indicated by anything which we perceive. This doctrine was naturally espoused with warmth by the extreme uniformitarian school, which required an unlimited duration of time for the accomplishment of such slow and quiet cycles of change as they conceived to be alone recognisable in the records of the earth's past history.

It was Lord Kelvin who, in the writings to which I have already referred, first called attention to the fundamentally erroneous nature of these conceptions. He pointed out that, from the high internal temperature of our globe, increasing inwards as it does, and from the rate of loss of its heat, a limit may be fixed to the planet's antiquity. He showed that, so far from there being no sign of a beginning, and no prospect of an end to the present economy, every lineament of the solar system bears witness to a gradual dissipation of energy from some definite starting-point. No very precise data were then, or indeed are now, available for computing the interval which has elapsed since that remote commencement, but he estimated that the surface of the globe could not have consolidated less than twenty millions of years ago, for the rate of increase of temperature inwards would in that case have been higher than it actually is; nor more than 400 millions of years ago, for then there would have been no sensible increase at all. He was inclined, when first dealing with the subject, to believe that, from a review of all the evidence then available, some such period as 100 millions of years would embrace the whole geological history of the globe.

It is not a pleasant experience to discover that a fortune which one has unconcernedly believed to be ample has somehow taken to itself wings and disappeared. When the geologist was suddenly awakened by the energetic warning of the physicist, who assured him that he had enormously overdrawn his account with past time, it was but natural under the circumstances that he should think the accountant to be mistaken, who thus returned to him dishonoured the large drafts he had made on eternity. He saw how wide were the limits of time deducible from physical considerations, how vague the data from which they had been calculated. And though he could not help admitting that a limit must be fixed beyond which his chronology could not be extended, he consoled himself with the reflection that after all a hundred millions of years was a tolerably ample period of time, and might possibly have been quite sufficient for the transaction of all the prolonged sequence of events recorded in the crust of the earth. He was therefore disposed to acquiesce in the limitation thus imposed upon geological history.

But physical inquiry continued to be pushed forward with regard to the early history and the antiquity of the earth. Further consideration of the influence of tidal friction in retarding the earth's rotation, and of the sun's rate of cooling, led to sweeping reductions of the time allowable for the evolution of the planet. The geologist found himself in the plight of Lear when his bodyguard of one hundred knights was cut down. "What need

you five-and-twenty, ten or five?" demands the inexorable physicist, as he remorselessly strikes slice after slice from his allowance of geological time. Lord Kelvin is willing, I believe, to grant us some twenty millions of years, but Professor Tate would have us content with less than ten millions.

In scientific as in other mundane questions there may often be two sides, and the truth may ultimately be found not to lie wholly with either. I frankly confess that the demands of the early geologists for an unlimited series of ages were extravagant, and even, for their own purposes, unnecessary, and that the physicist did good service in reducing them. It may also be freely admitted that the latest conclusions from physical considerations of the extent of geological time require that the interpretation given to the record of the rocks should be rigorously revised with the view of ascertaining how far that interpretation may be capable of modification or amendment. But we must also remember that the geological record constitutes a voluminous body of evidence regarding the earth's history which cannot be ignored, and must be explained in accordance with ascertained natural laws. If the conclusions derived from the most careful study of this record cannot be reconciled with those drawn from physical considerations, it is surely not too much to ask that the latter should be also revised. It has been well said that the mathematical mill is an admirable piece of machinery, but that the value of what it yields depends upon the quality of what is put into it. That there must be some flaw in the physical argument I can, for my own part, hardly doubt, though I do not pretend to be able to say where it is to be found. Some assumption, it seems to me, has been made, or some consideration has been left out of sight, which will eventually be seen to vitiate the conclusions, and which when duly taken into account will allow time enough for any reasonable interpretation of the geological record.

In problems of this nature, where geological data capable of numerical statement are so needful, it is hardly possible to obtain trustworthy computations of time. We can only measure the rate of changes in progress now, and infer from these changes the length of time required for the completion of results achieved by the same processes in the past. There is fortunately one great cycle of movement which admits of careful investigation, and which has been made to furnish valuable materials for estimates of this kind. The universal degradation of the land, so notable a characteristic of the earth's surface, has been regarded as an extremely slow process. Though it goes on without ceasing, yet from century to century it seems to leave hardly any perceptible trace on the landscapes of a country. Mountains and plains, hills and valleys, appear to wear the same familiar aspect which is indicated in the oldest pages of history. This obvious slowness in one of the most important departments of geological activity doubtless contributed in large measure to form and foster a vague belief in the vastness of the antiquity required for the evolution of the earth.

But, as geologists eventually came to perceive, the rate of degradation of the land is capable of actual measurement. The amount of material worn away from the surface of any drainage-basin and carried in the form of mud, sand, or gravel by the main river into the sea, represents the extent to which that surface has been lowered by waste in any given period of time. But denudation and deposition must be equivalent to each other. As much materials must be laid down in sedimentary accumulations as has been mechanically removed, so that in measuring the annual bulk of sediment borne into the sea by a river, we obtain a clue not only to the rate of denudation of the land, but also to the rate at which the deposition of new sedimentary formations takes place.

As might be expected, the activities involved in the lowering of the surface of the land are not everywhere equally energetic. They are naturally more vigorous

where the rainfall is heavy, where the daily range of temperature is large, and where frosts are severe. Hence they are obviously much more effective in mountainous regions than on plains; and their results must constantly vary, not only in different basins of drainage, but even, and sometimes widely, within the same basin. Actual measurement of the proportion of sediment in riverwater shows that while in some cases the lowering of the surface of the land may be as much as 1-730th of a foot in a year, in others it falls as low as 1-6800. In other words, the rate of deposition of new sedimentary formations, over an area of sea-floor equivalent to that which has yielded the sediment, may vary from one foot in 730 years to one foot in 6800 years.

If now we take these results and apply them as measures of the length of time required for the deposition of the various sedimentary masses that form the outer part of the earth's crust, we obtain some indication of the duration of geological history. On a reasonable computation these stratified masses, where most fully developed, attain a united thickness of not less than 100,000 feet. If they were all laid down at the most rapid recorded rate of denudation, they would require a period of seventy-three millions of years for their completion. If they were laid down at the slowest rate they would demand a period of not less than 680 millions.

But it may be argued that all kinds of terrestrial energy are growing feeble, that the most active denudation now in progress is much less vigorous than that of bygone ages, and hence that the stratified part of the earth's crust may have been put together in a much briefer space of time than modern events might lead us to suppose. Such arguments are easily adduced and look sufficiently specious, but no confirmation of them can be gathered from the rocks. On the contrary, no one can thoughtfully study the various systems of stratified formations without being impressed by the fulness of their evidence that, on the whole, the accumulation of sediment has been extremely slow. Again and again we encounter groups of strata composed of thin paper-like laminae of the finest silt, which evidently settled down quietly and at intervals on the sea bottom. We find successive layers covered with ripple marks and sun cracks, and we recognise in them memorials of ancient shores where sand and mud tranquilly gathered as they do in sheltered estuaries at the present day. We can see no proof whatever, nor even any evidence which suggests, that on the whole the rate of waste and sedimentation was more rapid during Mesozoic and Palaeozoic time than it is to-day. Had there been any marked difference in this rate from ancient to modern times, it would be incredible that no clear proof of it should have been recorded in the crust of the earth.

But in actual fact the testimony in favour of the slow accumulation and high antiquity of the geological record is much stronger than might be inferred from the mere thickness of the stratified formations. These sedimentary deposits have not been laid down in one unbroken sequence, but have had their continuity interrupted again and again by upheaval and depression. So fragmentary are they in some regions that we can easily demonstrate the length of time represented there by still existing sedimentary strata to be vastly less than the time indicated by the gaps in the series.

There is yet a further and impressive body of evidence furnished by the successive races of plants and animals which have lived upon the earth and have left their remains sealed up within its rocky crust. No one now believes in the exploded doctrine that successive creations and universal destructions of organic life are chronicled in the stratified rocks. It is everywhere admitted that from the remotest times up to the present day there has been an onward march of development, type succeeding type in one long continuous progression. As to the rate of this evolution, precise data are wanting. There is, however, the important negative argument furnished by

the absence of evidence of recognisable specific variations of organic forms since man began to observe and record. We know that within human experience a few species have become extinct, but there is no conclusive proof that a single new species has come into existence, nor are appreciable variations readily apparent in forms that live in a wild state. The seeds and plants found with Egyptian mummies, and the flowers and fruits depicted on Egyptian tombs, are easily identified with the vegetation of modern Egypt. The embalmed bodies of animals found in that country show no sensible divergence from the structure or proportions of the same animals at the present day. The human races of Northern Africa and Western Asia were already as distinct when portrayed by the ancient Egyptian artists as they are now, and they do not seem to have undergone any perceptible change since then. Thus a lapse of four or five thousand years has not been accompanied by any recognisable variation in such forms of plant and animal life as can be tendered in evidence. Absence of sensible change in these instances is, of course, no proof that considerable alteration may not have been accomplished in other forms more exposed to vicissitudes of climate and other external influences. But it furnishes at least a presumption in favour of the extremely tardy progress of organic variation.

If, however, we extend our vision beyond the narrow range of human history, and look at the remains of the plants and animals preserved in those younger formations which, though recent when regarded as parts of the whole geological record, must be many thousands of years older than the very oldest of human monuments, we encounter the most impressive proofs of the persistence of specific forms. Shells which lived in our seas before the coming of the Ice Age present the very same peculiarities of form, structure, and ornament which their descendants still possess. The lapse of so enormous an interval of time has not sufficed seriously to modify them. So, too, with the plants and the higher animals which still survive. Some forms have become extinct, but few or none which remain display any transitional gradations into new species. We must admit that such transitions have occurred, that indeed they have been in progress ever since organised existence began upon our planet, and are doubtless taking place now. But we cannot detect them on the way, and we feel constrained to believe that their march must be excessively slow.

There is no reason to think that the rate of organic evolution has ever seriously varied; at least no proof has been adduced of such variation. Taken in connection with the testimony of the sedimentary rocks, the inferences deducible from fossils entirely bear out the opinion that the building up of the stratified crust of the earth has been extremely gradual. If the many thousands of years which have elapsed since the Ice Age have produced no appreciable modification of surviving plants and animals, how vast a period must have been required for that marvellous scheme of organic development which is chronicled in the rocks!

After careful reflection on the subject, I affirm that the geological record furnishes a mass of evidence which no arguments drawn from other departments of Nature can explain away, and which, it seems to me, cannot be satisfactorily interpreted save with an allowance of time much beyond the narrow limits which recent physical speculation would concede.

I have reserved for final consideration a branch of the history of the earth which, while it has become, within the lifetime of the present generation, one of the most interesting and fascinating departments of geological inquiry, owed its first impulse to the far-seeing intellects of Hutton and Playfair. With the penetration of genius these illustrious teachers perceived that if the broad masses of land and the great chains of mountains owe their origin to stupendous movements which from time to time have convulsed the earth, their details of contour must

be mainly due to the eroding power of running water. They recognised that as the surface of the land is continually worn down, it is essentially by a process of sculpture that the physiognomy of every country has been developed, valleys being hollowed out and hills left standing, and that these inequalities in topographical detail are only varying and local accidents in the progress of the one great process of the degradation of the land.

From the broad and guiding outlines of theory thus sketched we have now advanced amid ever-widening multiplicity of detail into a fuller and nobler conception of the origin of scenery. The law of evolution is written as legibly on the landscapes of the earth as on any other page of the Book of Nature. Not only do we recognise that the existing topography of the continents, instead of being primeval in origin, has gradually been developed after many precedent mutations, but we are enabled to trace these earlier revolutions in the structure of every hill and glen. Each mountain-chain is thus found to be a memorial of many successive stages in geographical evolution. Within certain limits, land and sea have changed places again and again. Volcanoes have broken out and have become extinct in many countries long before the advent of man. Whole tribes of plants and animals have meanwhile come and gone, and in leaving their remains behind them as monuments at once of the slow development of organic types, and of the prolonged vicissitudes of the terrestrial surface, have furnished materials for a chronological arrangement of the earth's topographical features. Nor is it only from the organisms of former epochs that broad generalisations may be drawn regarding revolutions in geography. The living plants and animals of to-day have been discovered to be eloquent of ancient geographical features that have long since vanished. In their distribution they tell us that climates have changed, that islands have been disjoined from continents, that oceans once united have been divided from each other, or once separate have now been joined; that some tracts of land have disappeared, while others for prolonged periods of time have remained in isolation. The present and the past are thus linked together not merely by dead matter, but by the world of living things, into one vast system of continuous progression.

In this marvellous increase of knowledge regarding the transformations of the earth's surface, one of the most impressive features, to my mind, is the power now given to us of perceiving the many striking contrasts between the present and former aspects of topography and scenery. We seem to be endowed with a new sense. What is seen by the bodily eye—mountain, valley, or plain—serves but as a veil, beyond which, as we raise it, visions of long-lost lands and seas rise before us in a far-retreating vista. Pictures of the most diverse and opposite character are beheld, as it were, through each other, their lineaments subtly interwoven and even their most vivid contrasts subdued into one blended harmony. Like the poet, "we see, but not by sight alone"; and the "ray of fancy" which, as a sunbeam, lightened up his landscape, is for us broadened and brightened by that play of the imagination which science can so vividly excite and prolong.

Admirable illustrations of this modern interpretation of scenery are supplied by the district wherein we are now assembled. On every side of us rise the most convincing proofs of the reality and potency of that ceaseless sculpture by which the elements of landscape have been carved into their present shapes. Turn where we may, our eyes rest on hills that project above the lowland, not because they have been upheaved into these positions, but because their stubborn materials have enabled them better to withstand the degradation which has worn down the softer strata into the plains around them. Inch by inch the surface of the land has been lowered, and each hard rock successively laid bare has communicated its own characteristics of form and colour to the scenery.

If, standing on the Castle Rock, the central and oldest site in Edinburgh, we allow the bodily eye to wander over the fair landscape, and the mental vision to range through the long vista of earlier landscapes which science here reveals to us, what a strange series of pictures passes before our gaze! The busy streets of to-day seem to fade away into the mingled copsewood and forest of pre-historic time. Lakes that have long since vanished gleam through the woodlands, and a rude canoe pushing from the shore startles the red deer that had come to drink. While we look, the picture changes to a polar scene, with bushes of stunted Arctic willow and birch, among which herds of reindeer browse and the huge mammoth makes his home. Thick sheets of snow are draped all over the hills around, and far to the north-west the distant gleam of glaciers and snow-fields marks the line of the Highland mountains. As we muse on this strange contrast to the living world of to-day the scene appears to grow more Arctic in aspect, until every hill is buried under one vast sheet of ice, 2000 feet or more in thickness, which fills up the whole midland valley of Scotland and creeps slowly eastward into the basin of the North Sea. Here the curtain drops upon our moving pageant, for in the geological record of this part of the country an enormous gap occurs before the coming of the Ice Age.

When once more the spectacle resumes its movement the scene is found to have utterly changed. The familiar hills and valleys of the Lothians have disappeared. Dense jungles of a strange vegetation—tall reeds, club-mosses, and tree-ferns—spread over the steaming swamps that stretch for leagues in all directions. Broad lagoons and open seas are dotted with little volcanic cones which throw out their streams of lava and showers of ashes. Beyond these, in dimmer outline and older in date, we descrie a wide lake or inland sea, covering the whole midland valley and marked with long lines of active volcanoes, some of them several thousand feet in height. And still further and fainter over the same region, we may catch a glimpse of that still earlier expanse of sea which in Silurian times overspread most of Britain. But beyond this scene our vision fails. We have reached the limit across which no geological evidence exists to lead the imagination into the primeval darkness beyond.

Such in briefest outline is the succession of mental pictures which modern science enables us to frame out of the landscapes around Edinburgh. They may be taken as illustrations of what may be drawn, and sometimes with even greater fulness and vividness, from any district in these islands. But I cite them especially because of their local interest in connection with the present meeting of the Association, and because the rocks that yield them gave inspiration to those great masters whose claims on our recollection, not least for their explanation of the origin of scenery, I have tried to recount this evening. But I am further impelled to dwell on these scenes from an overmastering personal feeling to which I trust I may be permitted to give expression. It was these green hills and grey crags that gave me in boyhood the impulse that has furnished the work and joy of my life. To them, amid changes of scene and surroundings, my heart ever fondly turns, and here I desire gratefully to acknowledge that it is to their influence that I am indebted for any claim I may possess to stand in the proud position in which your choice has placed me.

Hydrogen Sulphide Free from Arsenic.—H. Habermann (*Chemiker Zeitung*).—The author mixes 1 part by weight of calcium sulphide and 2 parts crystallised magnesium chloride with as much water as will form a thin paste, and warms at first gently and afterwards more strongly. Habermann has also proposed to free hydrogen sulphide from traces of arsenic by a passage over iodine, and then through water in a washing-bottle. He proposes a similar treatment for purifying hydrogen from hydrogen arsenide, phosphide, and sulphide.

NEW METHOD OF PRODUCING GEMS ARTIFICIALLY.

By JAMES MORRIS.

It has been claimed by a French *savant* that chemistry is a French science. While this very broad claim cannot be conceded in its entirety, it may well be admitted that the production of gems artificially is a French domain, and that the Paris specialists have up till now led the way in this field of research and synthesis. In how far the French, or any other methods, are the methods of nature, can be determined only by further experiment, and by study of, and comparison with, natural phenomena. It is at least likely that the most natural method will be the most successful one in practice.

In his large work on mineralogy, Quenstedt remarks in connection with the experiments of Senarmont on the artificial production of quartz, "Allein dennoch bleibt noch Natur unsere Lehrmeisterin."

It is a curious fact that many of the most valuable gems are found in nature together, and it almost seems as if in the chemistry of the earth's crust a few generic processes had determined the formation of groups of crystals, both of the noble class and of the more ordinary kinds.

This rule is sometimes so marked that the presence of one crystal is almost a sure indication that a certain other crystal is not far away. Thus, in the diamond fields of Brazil crystals of anatase accompanied the diamonds, as a slave his master, and were thus termed by the Spaniards "captivos."

Although I am not yet in a position to publish the method of production which I follow, it may for the present be stated that the process is a simple one, and that at least many analogies point to the probability of its being one of the natural and generic processes referred to above.

The bulk of the products consist of rounded and compact crystals, composed entirely or chiefly of alumina. Individuals have been formed over one-sixteenth of an inch in diameter, and others approaching that size in very large numbers. The most of them are transparent, and by subsequent prolonged ignition with nitrate of cobalt, followed by heating in acid, some were found to have taken on the blue colour. Other tests were also applied. They were very hard, and I believe that I am justified, in a mineralogical sense, in calling the transparent crystals colourless sapphires.

In future experiments the colouring-matters will be added at an early stage of the process. They contain little or no silica. The crystals act in varying degrees on polarised light, and there are specimens which remain quite dark on revolution between the prisms.

It is not impossible that these latter are spinels, but many things point to at least some of them being diamonds. They are smaller, and much fewer in number than the chief product, and I have not yet exposed any of them individually to destructive tests. It is a case in which chemical analysis, applied to the crystals *en masse*, is not sufficient.

The sparkle of some of these small crystals is magnificent. Carbon was present in the production of all the crystals, and some of the aluminous ones contain a little of that element. C. Greville Williams found a small amount of carbon in beryls and emeralds. Luzy has recently shown that carbon is directly soluble in fused mineral matter.

It is a curious fact that in the "pipes" in South Africa garnets and other more or less noble crystals accompany the diamond. Had less silica been present it is not unlikely that rubies and sapphires would also have been formed. The manner in which some of my products cut glass is remarkable. They do not merely furrow it, but produce a deep fracture, very suggestive of diamond, or of some body containing carbon in the diamond form.

The noble nature of the crystals is beyond doubt. Some which I have tested are more infusible than platinum. I have specimens half embedded in the platinum which had been fused. The crystals showed merely slight softening. On prolonged ignition at a somewhat lower, but still very high, temperature, they became coated with microscopic crystals of platinum. Some of these were thin, hexagonal plates of wonderful beauty.

Mr. Joly, of Dublin, was perhaps the first to bring prominently before chemists the considerable volatility of platinum, even under its melting-point. He obtained similar crystals on strongly igniting fragments of quartz on his platinum ribbon.

Among the tests used to indicate the presence of carbon in the aluminous crystals, the following ocular proof is very strong. Some of the crystals were fused in borax in a small platinum capsule. In the fused mass there remained a few skeletal forms having a cokey appearance. This cokey matter was afterwards treated with fluoride of ammonium and with acid. It was neither dissolved nor even dimmed. Silica in such a physical condition would have disappeared.

The evident presence of carbon in some of the products makes the likelihood of the small, singly refractive crystals, being not spinels, but diamonds, all the greater.

I hope to be able, at a not too distant date, to say something about the genesis of the crystals, and to communicate the results of further investigation. I shall also try to arrange some differential experiments for the purpose of increasing the amount of carbon in the crystals, both collectively and individually.

217, West George Street, Glasgow.

CAN ARSENIC BE QUANTITATIVELY VOLATILISED AS ARSENIC HYDRIDE?*

By F. W. SCHMIDT.

THE question whether arsenic can be quantitatively volatilised as arseniuretted hydrogen has often been discussed. It was natural to utilise the beautiful reaction for quantitative determinations in which arseniuretted hydrogen in contact with a dilute solution of silver is transformed into arsenious acid and metallic silver. But in by far the most cases the researches undertaken for this purpose have led to no result, since it was not found practicable to convert entirely either arsenic or antimony into volatile hydrogen compounds, though we find in literature indications that this has been effected in certain cases, especially when the quantities of arsenic were only small. Still no decisive conclusion was reached, and Fresenius pronounces a severe condemnation (*Lehrbuch der Quantitativen Analyse*, vol. i., 641), on all gravimetric processes founded upon the volatility of arseniuretted and antimonuretted hydrogen.

If I felt induced to resume experiments in this direction it was because an observation had shown that the entire arsenic present in commercial zinc-powder could be volatilised as arseniuretted hydrogen on treatment with hydrochloric acid. The following method was therefore adopted.

In the first place the accuracy of the above mentioned observation had to be quantitatively confirmed. 10 grms. of commercial zinc-powder were carefully dissolved in concentrated nitric acid (concentrated acid was used to prevent the volatilisation of traces of arsenic), the nitric acid present was expelled by evaporating down the solution obtained on the water-bath along with concentrated hydrochloric acid, and after reducing the arsenic acid by means of ferrous chloride the arsenic was distilled over as $AsCl_3$, according to E. Fischer's process. The arsenic

* Zeit. Anorganische Chemie.

was then determined in the distillate as trisulphide in the ordinary manner, whence it appeared that the commercial zinc-powder contained 0.04 per cent of metallic arsenic. As a check, a second portion of 10 grms. of the zinc-powder was submitted to the same operation, the AsCl_3 driven over on the addition of an excess of ferrous chloride, the distillate supersaturated with sodium bicarbonate, and the arsenic titrated by means of decinormal solution of iodine; the 1.16 c.c. of the solution consumed represent in the same manner 0.04 per cent of metallic arsenic.

As the proportion of arsenic in the zinc-powder was thus established, I could proceed to the determination of the arsenic in the form of arseniuretted hydrogen. The apparatus used for this purpose consisted of a round flask of the capacity of 200 c.c., fitted with a dropping funnel and a gas-delivery tube leading to three absorbent vessels each holding 100 c.c. The flask is placed upon a water-bath so that the reaction may be assisted by heat. The distance of the first absorption vessel from the round flask is at least 20 c.m., so that the liquid in the former may not become heated. The first absorption vessel is half filled with a solution of silver of the concentration 1:50; the second contains silver solution of the concentration 1:10, and the third contains bromohydrochloric acid. Ten grms. of the commercial zinc-powder were weighed into the round flask; the substance was moistened through with water, the apparatus is connected together, and hydrochloric acid (1 vol. concentrated acid diluted with 1 vol. water), is gradually introduced by the dropping funnel. The gas liberated at once deposited black metallic silver in the first absorption vessel. As soon as the escape of gas became sluggish the flame was lighted beneath the water-bath, and when the zinc-powder was fully dissolved a slow current of hydrogen previously washed in silver solution (1:10), and consequently free from arsenic, was passed through the apparatus for about half an hour so as to sweep the last traces of arseniuretted hydrogen out of the round flask. The contents of the third absorption vessel, and the liquid in the round flask, were found on careful examination utterly free from arsenic; all the arsenic, therefore, as in the first observation, had been volatilised as a hydrogen compound, and at the same time the transformation of the arseniuretted hydrogen with the silver solution was completed in the second absorption vessel, so that the third contained not a trace of arsenic. From the contents of the first and second absorbent vessel, the excess of silver was separated by means of sodium chloride, and the arsenic in the filtrate from the silver chloride, after an addition of sodium bicarbonate, was titrated with decinormal solution of iodine. There were again used, until a blue colour appeared, 1.16 c.c. of the standard solution corresponding to 0.04 per cent of metallic arsenic in the commercial zinc powder.

This result rendered it very probable that the complete volatilisation of the arsenic from the zinc powder in the state of arseniuretted hydrogen depends on the presence of the arsenic in the zinc powder as a zinc arsenide, or else in an exceedingly finely divided metallic state which energetically assists the quantitative conversion of the arsenic into its hydrogen compound. A quantitative volatilisation must therefore be attainable also in other cases if the arsenic is converted into a state analogous to combination or to fine metallic sub-division.

(To be continued).

A Closure for Burettes without a Cock.—Dannbacher (*Pharm. Central Halle*).—The arrangement consists of two perforated plates of wood rather elevated at the margin and fixed upon the ends of the burette and the outflow tube, both previously covered with a caoutchouc tube. When fixing the wooden plates the flexible tube receives a slight tension, which suffices to press the wooden plates against each other, so that after any rotation they remain as they have last been placed.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Continued from p. 60).

II.—The Syrup to be Examined may Contain Starch Sugar.

IN this case a direct polarisation must first be made. If this gives a coefficient of purity above 70, further examination is unnecessary, as it would only tend to raise the coefficient, never to lower it.

If, however, the coefficient falls below 70, the presence of starch sugar is still possible. To determine whether any is present the syrup is inverted as in I., and made up to the mark.

It is then decolourised by adding $\frac{1}{2}$ to 1; in the case of dark syrups from 2 to 3 grms. of bone charcoal previously washed with hydrochloric acid or of charred blood. If the latter is used, its absorption factor for invert sugar must be previously determined, and a corresponding correction in the polarimetric reading made in case the left-handed rotation is to be estimated accurately. In the present case it is sufficient to approximately determine this rotation at about 20°. Experience has shown that unadulterated syrups do not always have a λ -rotation corresponding to 0.33 of the original right-handed rotation, but in all cases it is at least one-fifth of the original reading. A syrup polarising 55 directly should, after inversion, read at least -11, calculated for normal weight. If this syrup should read -10 or less, or should even rotate to the right, then it has been adulterated with starch sugar. When the absence of starch sugar has thus been proved, the syrup must be examined according to I.

If, however, starch-sugar is present, then we must arrive at the total sucrose by adding to the direct polarisation the invert sugar found by Fehling's solution. In this procedure the Fehling's solution is used according to Soxhlet's directions, but as the amount of solution taken by this author would not suffice for 10 grms. of substance, we have to make preliminary experiments to determine the quantity of syrup which should be taken. This is done most easily by diluting 10 grms. syrup to 100 c.c., placing 5 c.c. of Fehling's solution into several test-tubes, and adding successively 8, 6, 4, and 2 c.c. of the syrup solution. Upon boiling we will arrive at a point where the Fehling's solution is no longer decolourised. If this is the case with 6 c.c., then 6 grms. of substance are weighed out, dissolved in 50 c.c. of water, and 50 c.c. of Fehling's solution added. The whole is boiled for two minutes, and the analysis conducted as in the estimation of invert sugar.

The invert sugar is calculated according to Meissl's table. The following data concerning the use of the table are taken from the original article, "*Zeitschrift des Vereins für die Rübenzuckerindustrie des Deutschen Reiches*," 1883, p. 768:—

Let—

$$\text{I. } \frac{\text{Cu}}{2} = \text{approximate absolute amount invert sugar} = Z.$$

$$\text{II. } Z \times \frac{100}{p} = \text{approximate per cent invert sugar} = y.$$

$$\text{III. } \frac{100 \text{ Pol.}}{\text{Pol.} + y} = R, \text{ relative number for sucrose.}$$

$$100 - R = I, \text{ relative number for invert sugar.}$$

$$R : Z, \text{ relation of sucrose to invert sugar} = 6.$$

$$\text{IV. } \frac{\text{Cu}}{p} \times F = \text{correct percentage of invert sugar.}$$

In these formulæ Cu is the weighed copper, p the amount of substance taken, pol. the polarisation, Z facilitates reading the vertical column, and $R : Z$ the horizontal column of the following table.

To use the table find the columns agreeing most closely with the values found for Z and $R : Z$. When these columns meet, the value of factor F will be found.

Factors for the Determination of Invert Sugar in the presence of Sucrose.

Sucrose: invert sugar =	M.grms. invert sugar = Z.									
R: Z.	245.	225.	200.	175.	150.	125.	100.	75.	50.	
90:10	56.2	55.1	54.1	53.6	53.1	52.6	52.1	51.6	51.2	
91:9	56.2	55.1	54.1	53.6	52.6	52.1	51.6	51.2	50.7	
92:8	56.2	54.6	53.6	53.1	52.1	51.6	51.2	50.7	50.3	
93:7	55.7	54.1	53.6	53.1	52.1	51.2	50.7	50.3	49.8	
94:6	55.7	54.1	53.1	52.6	51.6	50.7	50.3	49.8	48.9	
95:5	55.7	53.6	52.6	52.1	51.2	50.3	49.4	48.9	48.5	
96:4			52.1	51.2	50.7	49.8	48.9	47.7	46.9	
97:3			50.7	50.3	49.8	48.9	47.7	46.2	45.1	
98:2			49.9	48.9	48.5	47.3	45.8	43.3	40.0	
99:1			47.7	47.3	46.5	45.1	43.3	41.2	38.1	

Factors = F.

Example.—The polarisation of a sugar is 86.4 and 3.256 grms. substance = p is equivalent to 0.290 grm. copper = Cu, then:—

$$\begin{aligned} \text{I. } \frac{\text{Cu}}{2} &= \frac{0.290}{2} = 0.145 = Z. \\ \text{II. } Z \times \frac{100}{p} &= 0.145 \times \frac{100}{3.256} = 4.45 = y. \\ \text{III. } \frac{100 \times \text{pol.}}{\text{Pol.} + y} &= \frac{86.4}{86.4 + 4.45} = 95.1 = R. \\ 100 - R &= 100 - 95.1 = Z; \quad R:Z = 95.1:4.9. \end{aligned}$$

By consulting the table we find that column 150 comes nearest to $Z = 145$, and column 95.5 is nearest to $R:Z = 92.1:4.9$.

Where these columns meet we find the factor 51.2, which enters into the last calculation.

$$\text{IV. } \frac{\text{Cu}}{p} \times F = \frac{0.290}{3.256} \times 51.2 = 4.56 \text{ per cent invert sugar.}$$

To convert this into saccharose, we subtract $\frac{1}{3}$; $4.56 - 0.23 = 4.33$; add this figure to the direct polarisation and calculate the coefficient of purity from this and the degree Brix.

III.—The Presence of Raffinose must be Considered.

If the chemist is required to consider the presence of raffinose he must proceed as follows:—

(a) The direct polarisation of the sugar is determined, as also (b) the indirect polarisation at exactly 20° C.

The same precautions must be taken in making the inversion as in I. and II. Half the normal weight is dissolved in 75 c.c. of water in a 100 c.c. flask, 5 c.c. hydrochloric acid (38.8 per cent HCl) added, and heated for seven and one-half to ten minutes to 60 to 70° C. After making up to the mark and clarifying with washed bone-black, the reading is taken at exactly 20° C. The following formula serves to calculate the result:—

$$Z (\text{sugar}) = \frac{0.5188 P - J}{0.845}, \text{ and } R (\text{raffinose}) = \frac{P - Z}{1.85};$$

when P = direct polarisation and J = invert reading for normal weight, the prefixed sign having been changed.

The invert sugar is determined as in other syrups. If the test described in Article A shows it to be present in quantities of less than 2 per cent, then it need not be further considered. Two per cent or more of invert sugar must be determined quantitatively according to Meissl's method, described in II., and calculated as saccharose. In finding the factor of this table, raffinose is to be considered as sucrose and Meissl's value. Pol. is therefore the sum of sucrose and raffinose. The coefficient of purity is calculated from the degree Brix and the total sucrose (that is, sucrose + invert sugar calculated to sucrose), the raffinose not being considered.

Example.—The examination of a syrup gave 85.6° Brix, 76.6 direct polarisation, —3 Pol. after inversion. By using the above formula we find 50.5 sucrose and 14 raffinose. There were also found 2.1 per cent sucrose as invert sugar. Therefore the total sucrose is 52.6 and the coefficient 61.4.

Rank deceptions might be practised by adding small amounts of starch sugar syrup to very pure syrups and requesting an examination with regard to raffinose present. In such cases the above method would cause an error in finding too small a sugar content and a considerable amount of raffinose corresponding to the starch sugar added.

The application of this method for the examination of syrups supposed to contain raffinose is hence only possible when no starch sugar is present. If starch sugar is known to be present, then the method described in II. must be used.

The estimation of starch sugar cannot be made exactly as described in II. for syrups in general, as syrups containing raffinose give a different invert reading.

If, therefore, a product is to be examined which is supposed to contain raffinose, it is best to use method No. III., and calculate sucrose and raffinose from this. The observed readings should not vary more than +5° from the calculated readings, otherwise starch sugar is certainly present and the raffinose formula no more applicable. In such a case the syrup must be examined according to II.

(To be continued.)

THE ACTION OF WATER UPON GLASS.

By F. MYLIUS and F. FOERSTER.

THE authors summarise their rough researches in the following propositions, which they consider proved by their own observations and those of Pfeiffer and Kohlrausch:—

1. The solution of glass in water depends on a decomposition in which, in the first place, free alkali appears.
2. The silica of the glass is secondarily dissolved by the free alkali.
3. The constituents of the solution vary according to the conditions of digestion.
4. The quantity of alkali which passes into solution from a given surface under given conditions is a measure for the attackability of the glass under these conditions.
5. The attackability of surfaces of glass by cold water decreases at first very rapidly with the duration of digestion, and subsequently approach constant values.
6. Different sorts of glass display a different persistence of the solution. (By this term Kohlrausch characterises the relation of its solubility after a prolonged digestion to its original solubility).
7. The attackability of glass increases very rapidly with a rising temperature.
8. The relation of the attackabilities of different kinds of glass depends on temperature.
9. From glasses of equal attackability unequal weights may pass into solution.
10. The attackability of good glass is decidedly decreased by a previous treatment with water.
11. The worse a glass the less its attackability is diminished by treatment with water.
12. The attackability of glass surfaces is modified by "weathering."
13. After treatment with water, surfaces of glass have the property of taking up alkali from the solutions which have been formed, and of giving it up again on renewed treatment with water.
14. Potash glasses are much more soluble than soda-glasses, but the differences disappear in proportion as the glass is richer in lime.
15. In the substance of glass vessels, which are not readily attacked by cold and hot water, the lime, alkalies, and silica must bear a certain proportion to each other.
16. Among the best known glasses plumbiferous flint glass is least soluble in water, but it is corroded at its surface and easily decomposed by acids.—*Zeit. Anal. Chemie.*

A REVISION OF THE ATOMIC WEIGHT
OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 58).

It has been said that these experiments were intended only for rough comparison. Since it appeared possible to apply a corresponding correction to the atomic weight of copper deduced from the oxide, it became important to make a more accurate series of determinations. The cupric oxide used in these final experiments represented three different specimens, similar to or identical with those used in Nos. 43, 45, 48, and 49.

Occluded Gas in Cupric Oxide.—Third Series.

Number of experiment.	CuO taken. Grms.	Gas evolved. [Apparatus.] C.c.	Temperature of gas. Centi- grade.	Atmospheric pressure. M.m.	Per cent of nitrogen in CuO by weight.	Per cent of oxygen in CuO by weight.
103.	1.84	1.38 (bulbs)	25°	757	0.080	0.003
104.	1.80	1.55 (flask)	22°	763	0.094	0.004
105.	1.30	1.10 (bulbs)	24°	760	0.090	0.004
Average					0.088	0.004

The cupric oxide of the last determination was ignited for three hours in a stream of air, and for twenty minutes in a stream of oxygen, at a medium red heat. It was impossible to determine whether the material had reached constant weight, for the hard glass tube in which the ignition was conducted was very much altered by the heat.

As might have been expected, the very pure cupric oxide employed in these experiments contained a slightly greater amount of occluded gas than the less carefully prepared material of the earlier experiments. Since the latest samples of material were precisely similar to those used in the quantitative analysis of cupric oxide, it is fitting that the latest correction should be applied to those quantitative results. The 2.97909 grms. of cupric oxide used in Experiments 48 and 49 must have contained 0.00276 gm. of occluded gas. That is to say, 2.97633 grms. of pure cupric oxide correspond to 2.37811 grms. of metallic copper. The difference between these weights now really represents the weight of combined oxygen present. The atomic weight of copper upon this basis is easily found to be 63.605.

Correcting the indirect results from the synthesis of cupric sulphate in the same way (see *ante*) the number 63.603 is obtained. Averaging this result with that immediately above, the value 63.604 is found as a mean of five determinations including two wholly distinct methods.

Since it is impossible to learn exactly the amount of gas occluded by Hampe's cupric oxide, the correction of his results will not be attempted. The residue left after the ignition of cupric sulphate can hardly contain any nitrogen; and this supposition more than accounts for the difference between the results of Baubigny's analysis and the present syntheses of cupric sulphate (see p. 21).

Upon referring to the other work upon the atomic weight of copper, it is apparent that nearly all the discrepancies have been explained. A portion of Millon and Commaillé's work consisted of weighing the water formed by the reduction of cupric oxide; the reason of the low result of this part of their work is not even now evident, but at the present day a discussion of the possible causes of its error would be unprofitable. Shaw's recent result,

which formerly ranked among the highest of the observed values, now appears among the lowest.

Evidently the occlusion of nitrogen by cupric oxide must have a very serious effect upon experiments in which oxygen is determined by the loss of weight of material prepared by the ignition of the basic nitrate; notably in the determination of the atomic weight of the element after the method of Dumas. When the oxide is obtained by the ignition of the metal in oxygen, the correction is of course inapplicable. Unfortunately, most of the experimenters upon the subject have omitted to state the source of their cupric oxide. The preparation used in the later experiments of Erdmann and Marchand (*Four. für Prakt. Chemie.*, xxvi., 461) must have contained nitrogen; and it will be remembered that the second series of his results gave a much higher result than the first.

In view of the correction, it is remarkable that the resultant atomic weight of oxygen in this case was not even higher than 16; for the correction is about five times as large as the amount necessary to account for the difference between 15.87 and that figure. From a difference either in the mode of preparation or in the temperature of ignition, the oxide used by Erdmann and Marchand must have contained much less nitrogen than the amount found in Experiments 103 to 105; or else some opposite error must have partially counterbalanced this one. Considering the remoteness of all the experiments, a present discussion of the results is unnecessary; but the conclusions are at least sufficient to throw a serious doubt upon the applicability of cupric oxide for a quantitative source of oxygen, as well as to support the modern low atomic weight of that element. The presence of nitrogen could not seriously influence the results of Keiser or those recently obtained here; and it is evident that the material used by Noyes could have contained no occluded gas.

The use of cupric oxide prepared from the nitrate must also introduce a serious error into organic nitrogen determinations after the method of Dumas, as Frankland and Armstrong have already pointed out. The usual "wire form" of cupric oxide is not subject to this cause of inaccuracy, however.

In the near future other oxides will be investigated at this laboratory with regard to their possible occlusion of gases.

(To be continued.)

ANALYSIS OF RUBBER GOODS.

By H. JOSHUA PHILLIPS, F.I.C., F.C.S.,
Analyst to the Great Eastern Railway.

THE following analysis recently made by the writer of an indiarubber mat that has been in constant use at one of the City hotels for over nine years may be of interest to some readers of the CHEMICAL NEWS:—

Moisture	0.50
Silica	1.38
Oxide of iron and alumina	0.70
Zinc oxide	3.51
Sulphur	3.97
Barium sulphate	3.74
Chalk	31.94
Caoutchouc	54.26
100.00	

The mat, which was originally 5-8ths of an inch thick, was very little the worse for wear, but had become somewhat brittle. A fracture viewed under a lens showed that the ingredients were not very homogeneously blended. A somewhat new departure in rubber mat-making is the insertion of layers of canvas with the object of preventing cracking, and this appears to answer well for the purpose.

Stratford, London.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxvi.

THE CHEMICAL NEWS.

VOL. LXVI., No. 1707.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. EDINBURGH, 1892.

By Prof. HERBERT McLEOD, F.R.S., F.C.S.,
President of the Section.

IN endeavouring to prepare myself to properly fulfil the duties of President of this Section, to which I have been elected, and for which honour I am much indebted to the council and members of the Association (although I am only too well aware that the position might have been more efficiently filled by many others), I naturally looked at the reports of the previous meetings held in Edinburgh in 1834, 1850, and 1871, and it appears that on the first two occasions an address was not given by the president, a custom the discontinuance of which I have, at the present moment, much reason to regret.

At the meeting in 1834 a committee was appointed consisting of Dr. Dalton, Dr. Hope, Dr. T. Thomson, Mr. Whewell, Dr. Turner, Professor Miller, Dr. Gregory, Dr. Christison, Mr. R. Phillips, Mr. Graham, Professor Johnston, Dr. Faraday, Professor Daniell, Dr. Clark, Professor Cumming, and Dr. Prout, to report at the next meeting their opinion on the adoption of an uniform set of chemical symbols, Dr. Turner to be secretary.

In the following year the report contains: "Report of the Committee on Chemical Notation." Dr. Turner, the chairman of the committee appointed to take into consideration the adoption of an uniform system of chemical notation, made a report to the following effect:—

"1. That the majority of the Committee concur in approving of the employment of that system of notation which is already in general use on the Continent, though there exists among them some difference of opinion on points of detail.

"2. That they think it desirable not to deviate in the manner of notation from algebraic usage except so far as convenience requires.

"3. That they are of opinion that it would save much confusion if every chemist would always state explicitly the exact quantities which he intends to represent by his symbols.

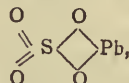
"Dr. Dalton stated to the Chemical Section his reasons for preferring the symbols which he had himself used from the commencement of the atomic theory in 1803 to the Berzelius system of notation subsequently introduced. In his opinion regard must be had to the arrangement and equilibrium of the atoms (especially elastic atoms) in every compound atom, as well as to their number and weights. A system either of arrangements without weights, or of weights without arrangements, he considered only half of what it should be."

We can all sympathise with the members of the section of 1834 in their desire to obtain a uniform system of chemical notation, for at that time several very different systems seem to have been in use. Although the report is a short one, it probably directed the attention of chemists to the desirability of avoiding confusion by the use of various systems, and since that period many advances have been made.

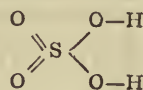
There is now little necessity for every chemist to "state explicitly the exact quantities which he intends to represent by his symbols," for the accurate determinations of atomic weights by many chemists—and we must not omit to mention the work of Stas (whose death we have had to deplore since the last meeting of the British Association)

—have given us a series of numbers which are in the hands of all chemists, so that, except in the cases where great refinement is requisite (or when the atomic weight has not been universally accepted), there is no need to state the values of the symbols.

That great advances have been made in chemical notation is well known to all; even in my own short experience I have had to learn several different methods. When I began to work at chemistry I was told that sulphate of lead was to be expressed by the formula PbO,SO_3 . Hofmann taught me that it should be $PbSO_4$; then Gerhardt doubled the atomic weights of oxygen and sulphur, and the formula became Pb_2SO_4 ; Cannizzaro showed that the atomic weight of lead should also be doubled, and the formula again became $PbSO_4$, but representing twice as much as formerly; then Frankland taught me to write SO_2Pb as the expression of the graphic formula—



which not only states that the compound contains 207 of lead, 32 of sulphur, and 64 of oxygen, but that the sulphur is hexad, and is combined with two atoms of dyad oxygen, and with a dyad compound radical containing one atom of lead and two of oxygen; and of all the formulæ just given this is the only one which satisfies the requirements which Dalton thought necessary in 1835, namely, to indicate not only the weights of the elements present, but also their arrangement. It may be objected that we do not know that this formula really represents the arrangements of the atoms in plumbic sulphate, but there can be very little doubt that the four atoms of oxygen in the compound are not all in the same condition, for if we examine the properties of sulphuric acid (from which the sulphate of lead is derived by the replacement of the hydrogen by lead), we find that two of the atoms of oxygen are more closely associated with the hydrogen than are the other two, and as there is some evidence, although perhaps not very conclusive, that sulphur may be capable of combining with six monad atoms, although no such compound is yet known, it does not seem unreasonable to suppose that sulphuric acid is really—



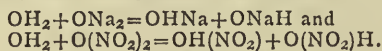
What the nature of the attraction that holds the atoms together may be is not known, but it is more probably of a character similar to that of gravity which holds together sun and planets, than of the nature of cohesion which would hold the atoms rigidly together; the atoms in each molecule are therefore most probably in a state of rotation around, or of vibration to and from, the central atom which holds them together. The pictorial representation in a plane does not therefore truly express the position of the atoms, but merely the relations existing between them. In organic chemistry the use of formulæ expressing such a relation has become indispensable, and in inorganic chemistry I believe such a system is very useful.

Recently this system has been found insufficient for the requirements of organic chemistry, and recourse has been had to the figure of a tetrahedron to represent the atom of carbon, other atoms being attached to the solid angles; in this way the position of the atoms in space is more or less expressed.

There are many cases, however, in which the atomicity theory fails us. At first it seemed probable that the atomicity of an element varied in pairs of attractions, that is, an element might be monad, triad, or pentad, but not dyad or tetrad; or it might be dyad, tetrad, or hexad, but not triad or pentad; but some great difficulties have been

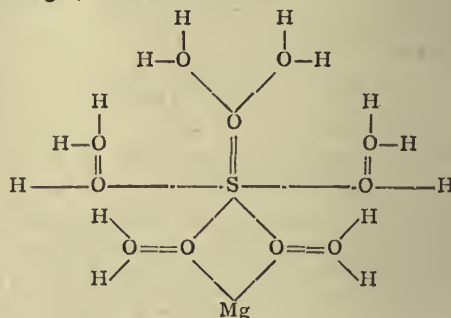
encountered. Thus nitrogen, which is pentad in ammoniac chloride and triad in ammonia, forms the compound nitric oxide, NO, in which it would appear to be dyad; it has been suggested, however, that in this body the nitrogen is really triad, and that it possesses a "free bond." Now the idea of a "free bond" seems contrary to the principles of atomicity, since it is on the belief that such a free bond is impossible that the explanation of the existence of elementary molecules is found, for it is said that when hydrogen is liberated two atoms unite to form a molecule, so that their mutual attractions may be satisfied. Nevertheless, nitric oxide is a very active body, uniting readily with other substances, so the free bond seems to be on the look out for other kinds of matter, but to have no attraction for the free bond of another molecule of nitric oxide. As the molecule of nitric peroxide is variable by alterations of temperature, being N_2O_4 at low and NO_2 at high temperatures, it seemed not impossible that at the ordinary atmospheric temperature nitric oxide was a simplified or dissociated molecule, and that if the temperature were sufficiently reduced it would be found that its molecule would be N_2O_2 , and thus it would contain triad nitrogen without a free bond. The density of the gas has, however, been determined at a temperature as low as -73° , and the molecule is still NO. Another important exception to the variation of the atomicity of an element in pairs was furnished by the investigations of Sir Henry Roscoe on the chlorides of vanadium; this element, which, from analogy, should be a triad or a pentad, appears to form a chloride of the composition VCl_4 . Again, the molecule of peroxide of chlorine is ClO_2 , which would make chlorine a tetrad or the compound must have a free bond.

Another set of phenomena which the atomicity theory will not explain is the existence of well-defined crystalline salts containing what is called water of crystallisation. This water is in many cases held with considerable pertinacity, the body appearing to be a veritable chemical compound. But water appears to be a saturated body, the attractions of the oxygen being satisfied by those of the hydrogen. It is true that water acts vigorously on other compounds, as on metallic oxides to form hydrates, and on some anhydrides to form acids, but these appear to be phenomena of double decomposition; thus the combination of water with sodic oxide and nitric anhydride respectively may be expressed by the equations—

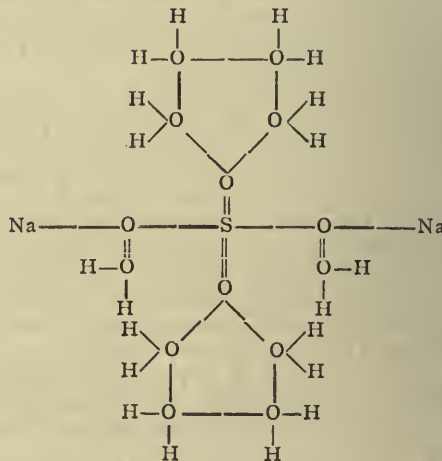


In the combination of water with an anhydrous salt, a phenomenon often accompanied by great rise of temperature, there does not appear to be a double decomposition. That there is a chemical combination of some sort is shown by the changes of properties produced, crystalline form and colour being both sometimes altered. Compounds so produced have been called "molecular compounds" to imply that saturated molecules are in some way or another combined, the combination being different from "atomic combination," in which the atoms are directly united according to their valencies. Another explanation has been suggested by assuming that there is some "residual affinity" not saturated by the constituents of the body, and that this residual affinity enables bodies to unite in a less stable manner than in most compounds. But are not these terms—"molecular combination" and "residual affinity"—analogous to the term "catalysis," merely words to express—not to explain—what we do not understand? If "residual affinity" really exists, it must reside in the oxygen of the water, or in the hydrogen, or in both; if so, what will happen to some of the complex constitutional formulæ of the organic chemist in which the carbon is tetrad, the oxygen dyad, and the hydrogen monad? If any of these elements have a residual affinity should we not expect to find additional unions between some of the atoms of the same molecule over and above those represented by the formula?

Oxygen may be tetrad, for which there is evidence in OAg_4 . Under these circumstances water is by no means a saturated compound, and there would be no difficulty in explaining the combination of water with oxygen salts. Thus crystallised magnesian sulphate, $MgSO_4 \cdot 7OH_2$, or $SOHoMgo$, $6OH_2$ would be—



and sodic sulphate, $Na_2SO_4 \cdot 10OH_2$:—



Even alum, with its 24 molecules of water of crystallisation, may be expressed by an appalling formula :—(See next page).

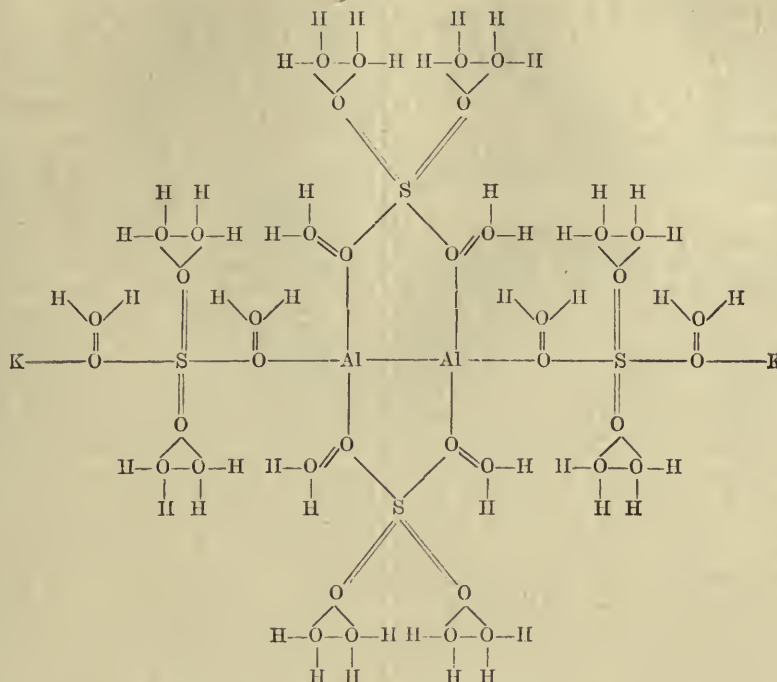
There is certainly a symmetry about the formula, and it will be found that 16 of the molecules of water are in a different position from the remaining 8; this probably has no significance, although Graham found that crystallised alum at a temperature of 61° lost 18 molecules of water; if he had used a temperature a few degrees lower he might have found that only 16 passed off!

By a little stretching of the imagination and altering the atomicities of the elements to suit each particular case, no doubt graphic formulæ might be made for all crystalline salts, but they would be perfectly artificial, and not much good is likely to come from the attempt.

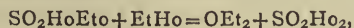
I fear we are driven to the conclusion that, notwithstanding all the progress that has been made in chemical science during the last fifty-eight years, we have not yet reached a method of notation that would have satisfied Dr. Dalton in 1834.

But since that time we have learnt that our formulæ ought to show even more than the number and position of the atoms of a compound; we should like them to indicate the amount of potential energy residing in a body, and our equations ought to indicate the amount of heat generated by a chemical change. Let us hope that before the next meeting of the British Association in Edinburgh these desirable developments will have been accomplished.

A short time ago I mentioned the word catalysis as



being employed to express certain chemical actions which cannot be explained. It is applied to those phenomena which take place in the presence of a body which appears to be entirely unchanged by the action. Happily these catalytic actions are being explained one after another, so that soon the name itself may become obsolete. An example of this action of presence may be given. When a mixture of sulphuric acid and alcohol is heated to a temperature of about 140° to 150° , ether passes over. Now alcohol contains C_2H_6O , and if from two molecules of alcohol one molecule of water is subtracted, a molecule of ether results: $2C_2H_6O = OH_2 + C_4H_{10}O$. As sulphuric acid is known to have a great attraction for water, it is easy to imagine that the acid combines with the water and ether passes off. But it is found that a small quantity of sulphuric acid at the temperature of 140° to 150° will transform a very large amount of alcohol into ether and water, much more than can be explained by assuming that the acid has combined with the water. If a mixture of sulphuric acid and alcohol is heated to a temperature of 140° to 150° , and alcohol allowed to flow into the liquid, a mixture of ether and water vapours passes over, and after a large quantity of alcohol has been transformed, the amount of sulphuric acid is found to be unaltered. At first glance this seems very difficult to explain, but on further investigation it is found that alcohol and sulphuric acid act one on another to form ethyl-sulphuric or sulphovinic acid: $SO_2HO_2 + EtHo = SO_2HOEtO + OH_2$; but when ethyl-sulphuric acid is heated with alcohol, ether is formed with the reproduction of sulphuric acid—



the sulphuric acid is then able to produce ethyl-sulphuric acid by acting on more alcohol, so a continuous production of ether and water takes place without loss of sulphuric acid. Another well-known action is the combination of oxygen and hydrogen under the influence of spongy platinum. In this case the platinum remains apparently unaltered, and is capable of causing the combination of any quantity of mixed gases. As spongy platinum possesses the power of absorbing large quantities of gases, it is usually said that the molecules of

oxygen and hydrogen are so much condensed in the platinum that they are brought within the sphere of one another's attractions, and consequently combine.

Another instance of an action of this kind is afforded by the oxidation of ammonia in the presence of chromic oxide. When ammoniac dichromate is heated an evolution of gas occurs, and a residue of chromic oxide is left which bears a striking resemblance to a mixture of black and green tea; when some of this substance is placed on a piece of wire gauze, heated, and then supported over a vessel containing a strong solution of ammonia, the oxide glows in a manner similar to the glowing of spongy platinum under the influence of a mixture of hydrogen and air. Under these conditions the chromic oxide facilitates the oxidation of the ammonia, but it becomes changed during the process; instead of having the appearance above described it acquires a bright green colour. Now, we know that chromium is capable of forming several combinations with oxygen. Is it therefore too much to suppose that the chromium is alternately oxidised by the oxygen of the air, and reduced by the hydrogen of the ammonia, so that although in the end it has the same composition as at the beginning, nevertheless it has been continuously decomposed and reproduced? Now, may not a similar change take place during the action of spongy platinum on a mixture of hydrogen and oxygen? The alteration of the platinum is very slight, but I believe I have observed a slight modification of the appearance of a fragment of spongy platinum, that was kept glowing by a small jet of purified hydrogen for some hours, the gas not being allowed to burn so as to heat the platinum to a very high temperature, the metal appears to be compacted and to be covered by minute spherules of glistening metal. Now, may not the platinum have entered into combination with one or other of the gases, and been subsequently reduced? If this is the true explanation, then we have in this case a continuous series of chemical changes and the "catalysis" is explained.

We all know the ease with which oxygen is obtained from potassic chlorate when heated with a small quantity of oxide of manganese; the quantity of peroxide is the

same at the end of the process as at the beginning, and it may be used over and over again to assist in the decomposition of fresh potassic chlorate. The oxide of manganese undergoes a molecular alteration; if a crystalline variety is employed, it is found at the end of the process to have been transformed into fine powder.

I hope I have proved to the satisfaction of my brother chemists that potassic permanganate is first formed and subsequently decomposed with the reproduction of manganese peroxide.

Oxide of cobalt possesses the remarkable property of decomposing solutions of hypochlorites at moderate temperatures with evolution of oxygen. For some time I have been endeavouring to find the explanation of the change, but hitherto without complete success. At first it seemed probable that an unstable cobaltate, analogous to a ferrate, was formed and decomposed at the temperature of the experiment. In fact, oxygen is evolved when chlorine is passed through a boiling solution of sodic hydrate containing ferric hydrate in suspension. But no evidence of the existence of a cobaltate could be found. When a cobaltous salt is added to an alkaline solution of a hypochlorite, a black precipitate is formed which is usually stated to be cobaltic hydrate, $\text{Co}_2\text{H}_2\text{O}_6$, but Vortmann has shown that when a cobaltous salt is mixed with a solution of iodine in potassic iodide, and the liquid rendered alkaline by sodic hydrate, the precipitate formed at a temperature between 50° and 60° approaches in composition the dioxide of cobalt, CoO_2 . He also found that the precipitate lost oxygen at the temperature of boiling water. I have repeated some of his experiments, and can quite confirm them, although I have not obtained an oxide containing quite as much oxygen as his richest oxide. The oxides I prepared rapidly effected the decomposition of a solution of sodic hypochlorite, and that without undergoing any loss of oxygen themselves; in fact, in the two experiments made, the cobalt compound contained a little more oxygen after boiling with the hypochlorite.

We have now many instances of the influence which small quantities of substances have upon chemical reactions. These influences may be more common than is generally supposed. The presence of a third body is frequently helpful in the combination of elements with one another: thus dry chlorine will not attack melted sodium or finely divided copper; an electric spark will not cause a dry mixture of carbonic oxide and oxygen to explode; carbon, phosphorus, and sulphur will not unite with dry oxygen, and as chemical science progresses we may find that many well-known actions are conditioned by the presence of minute traces of other matter which have hitherto escaped detection. We all know the profound alterations of the properties of substances by minute traces of impurities; less than one-tenth per cent of phosphorus will render steel unfit for certain purposes. The sapphire and ruby only differ from colourless alumina by the presence of traces of impurities hardly recognisable by chemical analysis. During this meeting we hope to have a contribution to the section on the influence of minute traces of what may be called impurities on the properties of different substances and their influence on chemical changes.

In this city, where the first public chemical laboratory was started in 1823 by Dr. Anderson, the assistant of Prof. Hope, it is hardly necessary to insist on the extreme importance of teaching chemistry by practical work, but unfortunately, even at the present time, endeavours are made to teach the subject by means of lectures (sometimes without experiments) or by reading. Those who are acquainted with chemistry well know the impossibility (this is hardly too strong a word) of learning the science, especially in the first stages, without actual experiment, by which a practical acquaintance with chemical phenomena is obtained. The attempt to learn chemistry without practical experience reminds one of the well-known story (for the truth of which I will not vouch) of a mathe-

matician who lectured on natural philosophy; he was visiting a foreign laboratory, and stopped before a piece of apparatus and asked what it was: on being told it was an air-pump he exclaimed: "Dear me! I have lectured on the air-pump for twenty-five years, and this is the first time I have seen one." It is problematical if his students can have derived much advantage from his lectures. Teaching of the kind to which reference has just been made is generally given to candidates for examinations who do not intend to take up chemistry as their chief subject. At the present time chemistry is required for entrance and preliminary examinations from many classes of students. There is no doubt that it is an excellent means of education, teaching a boy to observe and draw conclusions from his observations; but if he makes no observations it is little more than useless cram, the memory might as well be exercised by learning a novel by heart.

This imperfect mode of teaching chemistry arises principally from the difficulty of obtaining properly appointed laboratories in schools, in addition to which the very strong fumes are sometimes disagreeable, making it inconvenient to have them in or near a house, to say nothing of the possible dangers to the clothes and their contents; but there is no help for it, the teaching must be accompanied by experimental demonstration, as was indicated in the Reports on the teaching of chemistry which have been presented to this Association in former years. It must be admitted that examinations do not always discover the best student; many are capable of preparing for examinations with a small knowledge of their subject, others, with a good knowledge, fail from nervousness or other causes, but at the present time, examination, although far from perfect, is almost the only means we have of judging the fitness of the candidate. By properly selecting questions the examiner may, to a considerable extent, discourage cram; he should endeavour to find out what the pupils have actually seen, and to make them draw conclusions from facts which they have either themselves observed, or which have been described to them; it is only in this manner that chemistry can be used as a means of mental training.

These remarks do not apply to the education of students intending to make chemistry their profession, who have many opportunities in the large laboratories of Great Britain and the Continent of obtaining all the necessary instruction. The Institute of Chemistry, which was founded to improve the status and also the education of professional chemists, requires that its members should have a thoroughly scientific training. Before a candidate for the associateship is admitted to examination, he must bring evidence that he has passed satisfactorily through a systematic course of at least three years' study in the subjects of theoretical and practical chemistry, physics, and elementary mathematics, in some recognised college or school; and before admission to the fellowship he must have passed through three additional years of work in chemistry. It is to be hoped that an example of this kind will ultimately have a good effect in improving the modes of teaching the science in its elementary stages.

There is another class of workers in chemistry who must not be forgotten at the present time, as they have much influence on the life of the world, and have been working for ages, but have only recently been recognised. I mean those organisms which are included under the name of microbes. These organisms are capable of producing chemical changes which entirely surpass all the results hitherto obtained by the chemist in his laboratory. That the transformation of sugar into alcohol and carbonic anhydride in the ordinary process of fermentation is due to a living organism, has been known for some years; the important transformation of ammonia into nitrous and nitric acids in the soil has been shown to be due to organisms which have recently been investigated by many chemists; it is possible to transform ammonia into these acids in the laboratory by oxidation

under certain conditions and at a high temperature, whereas the organism does the work quite as efficaciously at the common temperature. Other organisms have the power of producing complex organic poisons by the alteration of some of the constituents of the animal body, and the relation of these products to the study of diseases is of the highest possible importance. As we hope to have a discussion on this interesting subject by many eminent authorities, both from the chemical and biological points of view, it will be unnecessary to pursue the subject further, unless it be to urge some of the younger chemists to work at the chemical aspect of bacteriology. They must be prepared for hard work and many disappointments, for the subject is undoubtedly a difficult one.

I cannot conclude this address without reference to the great loss which chemistry has sustained by the death of Prof. A. W. von Hofmann. I had the good fortune to be under him as student and assistant from 1856 until he left this country in 1865; all who worked with him must have been deeply impressed by his capacity for work and his power of inducing work in others. Although perhaps some of us did not appreciate this at the time, yet we feel we owe him a debt of gratitude for his having started us in the right way. The list of papers under his name in the Royal Society Catalogue up to the year 1883 is 299, written by himself alone, besides twenty-two joint papers. One of his characteristics which impressed me was his investigation for the purpose of furthering chemical knowledge without any view to practical applications, and I well remember his lecture at the Royal Institution, in 1862, on Mauve and Magenta (which owed so much of their success to his work), in which he produced the original specimen of benzene which had been obtained by Faraday from oil-gas in 1825. He pointed out that Faraday had prepared this substance and investigated its properties without ever supposing that it could have any practical application. The following is the concluding paragraph of the lecture:—

"Need I say any more? The moral of Mauve and Magenta is transparent enough; I read it in your eyes. We understand each other. Whenever in future one of your chemical friends, full of enthusiasm, exhibits and explains to you his newly-discovered compounds, you will not cool his noble ardour by asking him that most terrible of all questions, 'What is its use? Will your compound bleach or dye? Will it shave? May it be used as a substitute for leather?' Let him quietly go on with his work. The dye, the lather, the leather will make their appearance in due time. Let him, I repeat it, perform his task. Let him indulge in the pursuit of truth—of truth pure and simple—of truth not for the sake of Mauve, not for the sake of Magenta, let him pursue truth for the sake of truth."

This seems to me the true spirit of the scientific investigator, and in many cases the reward consists solely in the consciousness that the investigator has done his duty; in some cases the reward may take a more substantial form, and since the above paragraphs were written I have been informed that Professor von Hofmann has left a large fortune, the result of the applications of his discoveries in technical chemistry.

"Vivat Ars Chemica!"—The *Chemiker Zeitung* briefly notices a humorous work under this title from the pen of Dr. C. Geissler. We extract two distichs which we unfortunately cannot render in verse, and which show that even in the Vaterland the position of the chemical profession is not without its shadow-side: "My uncle, the chemist, has reached the age of forty, and last month he received his first salary." "My friend has already reached a tolerable position; no payment, heavy security, but free breathing." In a different direction is the advice: "If a girl pleases you, first test her mother with blue litmus-paper!" The work is published by Fesenfeld, of Freiberg, in Breisgau.

ADDRESS
TO THE
MATHEMATICAL AND PHYSICAL SECTION
OF THE
BRITISH ASSOCIATION,
EDINBURGH, 1892.

By Prof. ARTHUR SCHUSTER, Ph.D., F.R.S., F.R.A.S.,
President of the Section.

IN opening the proceedings of our Annual Meeting the temptation is great to look back on the year which has passed, and to select for special consideration such work published during its course as may seem to be of the greatest importance. I fear, however, that a year is too short a time to allow us to form a fair estimate of the value of a scientific investigation. The mushroom, which shoots up quickly, only to disappear again, impresses us more than the slow-growing seedling which will live to be a tree, and it is difficult to recognise the scientific fungus in its early stage. But, although I do not feel competent to give you a review of the progress made in our subject during the last twelve months, there is one event to which some allusion should be made. It has been the sad duty of many of my predecessors to announce the death of successful workers in the field of science, but I believe I am unique in having the pleasure of recording the birth of a scientific man. At the beginning of this year there came into the world a being so brilliant that he could, without preparation, take up the work of the most eminent man amongst us. Believers in the transmigration of souls have speculated on the fact that Galileo's death and Newton's birth fell within a year of each other; but no event has ever happened so striking as that which took place on the 1st of January, when the mantle of Sir William Thomson fell on the infant Lord Kelvin. Those who have attended these meetings will feel with me that the honour done to our foremost representative,—an honour which has been a source of pride and satisfaction to every student of science,—could not altogether remain unnoticed in the section which owes him so much.

We are chiefly concerned here with the increase of scientific knowledge, and we derive pleasure in contrasting the minor state of ignorance of our own time with that which prevailed a hundred years ago. But when we contrast at the same time the refined opportunities of a modern research laboratory with the crude conditions under which the experimentalist had to work at the beginning of the century, we may fairly ask ourselves whether it is possible by means of any systematic course of study, or by means of any organisation, to accelerate our progress into the dark continent of science. A number of serious considerations arise in connection with this subject, and though I am not going to weary you by attempting an exhaustive discussion, I should like to draw your attention to a few matters which seem to me to be well worthy of the consideration of this Association. Changes are constantly made and proposed in our existing institutions, or new ones are suggested which are to serve the purpose of a more rapid accumulation of knowledge. I need only allude to the alterations in the curriculum of the science school in our old Universities, made partly for the purpose of fitting their graduates for the conduct of original research, or to the national laboratory proposed by my predecessor in this chair for carrying out a certain kind of scientific investigation, which at present is left undone, or is done by private enterprise. Even our own Association has not escaped the evil eye of the reformer, and, like other institutions, it may be capable of improvement. But in choosing the direction in which a change may best be made, I think we may learn something from the way in which Nature improves its organisms. We are taught by biologists that natural selection acts by developing those qualities which enable

each species best to survive the struggle for existence; useless organs die off or become rudimentary. Nature teaches us, therefore, how a beautiful complex of beings, mutually dependent upon each other, is formed by improving those parts which are best and most useful, and letting the rest take care of itself. But in many of the changes which have been made or are proposed, the process of reform is very different. The weakest points are selected, our attention is drawn to some failure or something in which we are excelled by other nations, and attempts are made to cure what perhaps had better be left to become rudimentary. The proceeding is not objectionable as long as the nourishment which is applied to develop the weaker organs is not taken from those parts which we should specially take care to preserve. To apply these reflections to the question with which we are specially concerned, I should like to see it more generally recognised that although there is no struggle for existence between different nations, yet each nation, owing to a number of circumstances, possesses its own peculiarities, which render it better fitted than its neighbours to do some particular part of the work on which the progress of science depends. No country, for instance, has rivalled France in the domain of accurate measurement, with which the names of Regnault and Amagat are associated, and the International Bureau of Weights and Measures has its fitting home in Paris.* The best work of the German Universities seems to me to consist in the following up of some theory to its logical conclusions and submitting it to the test of experiment. I doubt whether the efforts to transplant the research work of German Universities into this country will prove successful. Does it not seem well to let each country take that share of work for which the natural growth of its character and its educational establishment best adapt it? Is it wise to remedy some weak point, to fill up undoubted gaps, if the soil that fills the gaps has to be taken from the hills and elevations which rise above the surrounding level?

As far as the work of this section is concerned, the strongest domain of this country has been that of mathematical physics. But it is not to this that I wish specially to refer. Look at the work done in Great Britain during the last two centuries; the work not only in physics, but in astronomy, chemistry, biology. Is it not true that the one distinctive feature which separates this from all other countries in the world is the prominent part played by the scientific amateur, and is it not also true that our modern system of education tends to destroy the amateur?

By amateur I do not necessarily mean a man who has other occupations and only takes up science in his leisure hours, but rather one who has had no academical training, at any rate in that branch of knowledge which he finally selects for study. He has probably been brought up for some profession unconnected with science, and only begins his study when his mind is sufficiently developed to form an entirely unbiassed opinion. We may, perhaps, best define an amateur as one who learns his science as he wants it and when he wants it. I should call Faraday an amateur. He would have been impossible in another country; perhaps he would be impossible in the days of the Science and Art Department. Other names will occur to you, the most typical and eminent being that of Joule. It is not my purpose to discuss why distinguished amateurs have been so numerous in this country, but I am anxious to point out that we are in danger of losing one great and necessary factor in the origination of scientific ideas.

One of the distinctive features of an amateur is this,

* Much of the good work done by this Bureau remains unknown, owing to the miserly way in which their publications are circulated. No copies are supplied even to the University libraries. The explanation, of course, is "want of funds." In other words, England, France, and Germany, together with other nations, unite to do a certain kind of work, but cannot afford to distribute a few copies of the publication to the public for whose benefit the work is undertaken.

that he carries not the weight of theories, often not the weight of knowledge, and, if I am right, there is a distinct advantage in having one section of scientific men beginning their work untrammelled by preconceived notions, which a systematic training in science is bound to instil. Whatever is taught in early age must necessarily be taught in a more or less dogmatic manner, and in whatever way it is taught, experience shows that it is nearly always received in a dogmatic spirit. It seems important, therefore, to confine the early training to those subjects in which preconceived notions are considered an advantage. It is to me an uncongenial task to sound a note of warning to our old Universities, for the chief difficulties in which they are placed at present are due to the fact that they have given way too much to outside advice; but I cannot help expressing a strong conviction that their highly specialised entrance examinations are a curse to all sound school education, and will prove a still more fatal curse to what concerns us most nearly, the progress of scientific knowledge. If school examinations could be more general, if scientific theories could only be taught at an age when a man is able to form an independent judgment, there might be some hope of retaining that originality of ideas which has been a distinctive feature of this country, and enabled our amateurs to hold a prominent position in the history of science. At present a knowledge of scientific theories seems to me to kill all knowledge of scientific facts.

It is by no means true that a complete knowledge of everything that has a bearing on a particular subject is always necessary to success in an original investigation. In many cases such knowledge is essential, in others it is a hindrance. Different types of men incline to different types of research, and it is well to preserve the dual struggle. The engine which works out the great problems of nature may be likened to a thermodynamic machine. The amateur supplies the steam and the Universities supply the cold water; the former, boiling over often with ill-considered and fanciful ideas, does not like the icy douche, and the professional scientist does not like the latent heat of the condensing steam, but nevertheless the hotter the steam and the colder the water the better works the machine. Sometimes it happens that boiler and cooler are both contained in the same brain, and each country can boast of a few such in a century, but most of us have to remain satisfied with forming only an incomplete part of the engine of research.

But while it is necessary to recognise the great work done by the unprofessional scientists, it seems not untimely to draw their attention to the damage done to themselves if they overstep their legitimate boundaries, and especially if they seek popular support for their theories, which have not received the approval of those who are competent to judge. An appeal from Alexander sober to Alexander drunk will not prove successful in the end.

The gradual disappearance of the amateur may be a necessary consequence of our increased educational facilities, and we must enquire whether any marked advantages are offered to us in exchange. There is one direction in which it would seem at first sight, at any rate, that a proper course of study could do much to facilitate the progress of research.

On another occasion I pointed out that two parties are necessary for every advance in science, the one that makes it and the one that believes in it. If the discoverer is born, and cannot be made, would it not be possible at any rate to train the judgment of our students so that they may form a sound opinion on the new theories and ideas which are presented to them? It is too early as yet to judge in how far our generation is better in this respect than the one that has gone before them, but on closer examination it does not seem to me to be obvious that any marked improvement is possible. Every new idea revolutionising our opinions on some important question must necessarily take time before it takes a proper hold on the

scientific world. Is it not true that any one who can at once see the full importance of a new theory, and accept it in place of the one in which he has been brought up, must stand at a height almost equal to that of the originator? The more startling and fresh the new conception, the fewer must be those who are ready to adopt it. But looking back at the history of science during the present century, is there much evidence that great discoveries have been seriously delayed by want of proper appreciation? We may hear of cases where important papers have been rejected by scientific societies, and occasionally a man of novel ideas may have been too much neglected by his contemporaries. I doubt whether such cases of apparent injustice can ever be avoided, and, simply looking back on the great changes involved in matters of primary importance, such as the undulatory theory of light, the conservation of energy, and the second law of thermodynamics, I cannot admit that there is much reason to be dissatisfied with the rate at which new theories have been received. Those who experience a temporary check, owing to the fact that public opinion is not ripe for their ideas, are often amply rewarded after a lapse of a few years. The disappointment which Joule may have felt during the time his views met with adverse criticisms from the official world of science was no doubt amply compensated by the pleasure with which he watched the subsequent progress of research in the new domain which his discoveries have opened out.

The point is not one of academic interest only, for the fear of repressing some important new discovery has a detrimental influence in another direction. The judgment of the scientific world seems to me to be tending too much towards leniency to apparently absurd theories, because there is a remote chance that they may contain some germ of real value. A new truth will not be found to suffer ultimately by adverse and even unreasonable criticism, while bad theories and bad reasoning, supported by the benevolent neutrality of those to whose judgment the scientific world looks for guidance, are harmful in many ways. They block the way to an independent advance and encourage hasty and ill-considered generalisations. The conclusions I should draw from the considerations I have placed before you are these: I believe that a reasonable censorship exercised by our scientific societies is good and necessary; that those whose fate it is to be called on to express an opinion on some work or theory should do so fearlessly according to their best judgment. Their opinion may be warped by prejudice, but I think it is better that they should incur the risk of being ultimately found to be wrong than that they should help in the propagation of bad reasoning. There is one matter, however, on which all opinions must agree. Worse than bad theory or logic is bad experimental work. Should we then not rigorously preserve any influence or incentive which encourages the beginner to avoid carelessness and to consider neither time nor trouble to secure accuracy? There is no doubt to my mind that the prospect of admission to the Royal Society has been most beneficial in this respect, and that the honourable ambition to see his paper published in the *Transactions* of that Society has preserved many a student from the premature publication of unfinished work.

(To be continued.)

The Dangers of Bacteriology.—According to a medical contemporary a London physician much devoted to the experimental study of microbia met with a shocking end. It was his custom, it appears, to carry in a bag cultures of pathogenic micro-organisms along with his lunch. Some bacillus or allied microbe found its way from the "culture" into the esculents, and the experimentalist paid for his indiscretion with his life. Without more discretion is exercised we shall have the enemies of Science agitating for legislative restrictions on bacteriological research.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Continued from p. 73).

IV.—Examination of Sugars for Raffinose.

THE method of examining syrups containing raffinose can be applied to sugars. The direct polarisation is taken in the usual manner, the indirect after inversion of one-half the normal weight just as directed for syrups under III. (b), and the content of sucrose and raffinose calculated by means of the formula given in III. Numerous experiments have shown this method to give reliable results. Thus there were found in mixtures of sucrose and raffinose:—

Mixture.		Found by the method.	
Sucrose.	Raffinose.	Sucrose.	Raffinose.
Per cent.	Per cent.	Per cent.	Per cent.
97'00	3'00	97'02	2'98
91'00	9'00	90'99	8'95
85'00	15'00	85'06	14'97

Though without doubt this method is very accurate, still a wide limit must be given for experimental errors on account of its novelty. A variation of 0'6 between the sucrose as calculated by the raffinose formula and that determined directly by polarisation has therefore been made the limit. Supposing, for instance, that the sucrose found by direct polarisation is 92'6 and that calculated by the formula 92 per cent, then we may suppose this difference to be caused by errors in the method. In such a case raffinose should be reported absent, and the direct polarisation used for the sugar content. If, however, only 91'9 per cent sucrose were found by the formula while the direct polarisation was 92'6, then the presence of raffinose can not be doubted. To avoid mistakes which may be caused by larger errors than 0'6 it is advisable to make a control determination in all cases where the difference is less than 1 per cent, and to base the presence or absence of raffinose upon the result of this control.

The above limit for errors will not influence the utility of the method, as the percentage of raffinose so far observed in high sugars always corresponded to more than 0'6 per cent of sucrose. No method has yet been proposed for the determination of smaller amounts of raffinose, and they may therefore be neglected. Scheibler's method of calculating small amounts of raffinose by supposing the organic substances not sugar to be equal to the ash is not accurate, as the excess of organic substance over ash is not known.

The method is, however, of value in cases where the result found by the formula varies comparatively little from the polarisation; for instance, corresponding to less than 1 per cent of sucrose. Here it will decide whether raffinose is present or whether the difference is caused by errors.

For this purpose the polarisation, moisture, and ash are determined, the organic substances not sugar taken as equal to the ash, and these four constituents added together. In all cases where raffinose is present the result will be over 100; if it falls below 100, raffinose may be considered absent. In the former case, the percentage of raffinose is calculated as follows:—

The percentage of water plus twice the ash is deducted from 100.

The result corresponds to the percentage of sucrose plus anhydrous raffinose. If we substitute a for the figure thus found, b for the direct polarisation, x for the sucrose present, and y for the raffinose present, then—

$$x + 1.85y = b$$

$$x + y = a$$

$$x \text{ (per cent sucrose)} = \frac{1.85a - b}{0.85}$$

$$y \text{ (per cent raffinose)} = \frac{a - 1.85a - b}{0.85}$$

* *Ann. Chim. Phys.*, [3], viii., 189, 205. See also Thudichum and Hake, *Fahresber.*, 1876, p. 966; and Johnson, *Fahresber.*, 1878, p. 286.
† Grünwald and Brauner have independently come to the conclusion that copper is a compound. If this is the case, the compound must be a very definite one. See *Chem. Soc. Abstracts*, 1890, p. 434.

change in the molecular weights of the standards of reference. Their experimental errors are far smaller than those of any of the others, and they involve the simplest and most direct processes, and the minimum number of necessary corrections. They are in no case computed by the objectionable method of difference. Finally, each one of the five is wholly independent of the weight of any copper compound whatsoever. These reasons constitute a sufficient ground for the separation of such results from the others.

Selected Series.

Ratio.	Salt decomposed.	If O=16'000, Cu=
I. 2Ag: Cu	AgNO ₃	63'601
II. 2AgBr: Cu	CuBr ₂	63'609
III. 2Ag: Cu	CuBr ₂	63'605
V. Na ₂ CO ₃ : Cu	CuSO ₄	63'600
VI. Na ₂ SO ₄ : Cu	CuSO ₄	63'607

Final average 63'604

If the oxygen is taken as 15'96, copper becomes 63'44. With oxygen 15'87, the value sinks to 63'09.

The mathematical discussion of these results is omitted, because it gives an exaggerated notion of the accuracy of the final average. The real probable error of this average is much more dependent upon the chemical purity of the electrolytic copper than upon the mere mechanical or experimental error with which alone the theory of least squares is competent to deal.

It is apparent that any one of the methods thoroughly investigated would have long ago afforded a fairly accurate knowledge of the atomic weight. Too much cannot be said against the multiplication of incomplete or carelessly obtained data; for such data carry with them not only uncertainty and confusion in the present, but also additional labour for a reviser in the future.

In the present investigation every reaction was assumed to involve some constant error, and every substance was assumed to contain some constant impurity, until a proof of the contrary was obtained. The research consisted, in fact, of a succession of mutual checks. The attempt was made to adopt precautions of a consistent order of refinement; and the still remaining causes of possible error have been carefully pointed out in the description. The not inconsiderable outlay of time, thought, and labour has been more than repaid by a conviction of the definiteness of the combining proportions which four years ago would have seemed to the writer impossible.

CAN ARSENIC BE QUANTITATIVELY
VOLATILISED AS ARSENIC HYDRIDE?*

By F. W. SCHMIDT.

(Concluded from p. 72).

To decide the correctness of this assumption there were introduced into the round flask of the apparatus described above, in addition to 30 grms. of pulverised zinc (zinc can be readily pulverised at 205°), 20 c.c. of a 1 per cent solution of arsenic containing 0'119 gm. of arsenic trioxide. (One gm. of commercial arsenious acid was dissolved in 100 c.c. of water; 20 c.c. of this solution consumed 40'2 c.c. decinormal iodine, corresponding to 0'199 gm. pure arsenic trioxide). The first absorption vessel was again charged with solution of silver 1:50, the second and the third with solution of silver at 1:10. After the apparatus was put together, hydrochloric acid (1:1) was again allowed to enter by means of the dropping-funnel as before, heat was applied until the zinc was entirely dissolved, and finally hydrogen free from arsenic was passed through the apparatus. The titration of the contents of

the absorption vessels (after precipitating the excess of silver by means of sodium chloride, &c.) used only 38'4 c.c. decinormal solution of iodine, which corresponds to 0'190 gm. arsenious acid; hence nearly 5 per cent of the original quantity of arsenic had remained in the round flask,—a result which confirms those formerly obtained by other authors.

Now came the decisive experiment, which was effected in the same manner with 20 c.c. of the 1 per cent solution of arsenic and 30 grms. of powdered zinc. When after heating for one hour the development of arsenic became sluggish, there was added to the contents of the round flask through the dropping-funnel an agent calculated to produce a state of the arsenic analogous to "combination or fine metallic distribution," i.e., a hydrochloric solution of stannous chloride (obtained by dissolving non-arseniferous tin foil in concentrated hydrochloric acid).

At the moment when this solution was dropped into the round flask there appeared at once a turbidity and then a dark precipitation. Both the turbidity and the precipitate disappeared in a few minutes after a little platinum chloride had been added to re-animate the development of hydrogen, and the liquid resumed its former appearance. The application of heat was still continued for about 15 minutes, and a current of hydrogen free from arsenic was then passed through the apparatus for about the same time. The titration of the contents of the absorption vessels then showed exactly 0'119 gm. of arsenious acid, since 40'2 c.c. of decinormal iodine solution were required for its conversion into arsenic acid. The residue in the round flask, on careful examination, showed no trace of an arsenical reaction.

Hence it follows with great probability that the above assumption is correct, though it is conceivable that the stannous chloride, in addition to its property of precipitating arsenic in a very finely-divided metallic condition, has also a catalytic action, since stannous chloride is continually regenerated in the liquid. Its *modus operandi* is further explained by the following observations. After proceeding as usual, and as the zinc in the round flask was chiefly dissolved, solution of stannous chloride containing 1 or 2 grms. of metallic tin was allowed to flow slowly in through the dropping funnel. The tin was by degrees rather quickly separated out as a spongy mass, which dissolved only slowly on the addition of concentrated hydrochloric acid, but could be easily dissolved with a brisk escape of hydrogen on the addition of a little platinum chloride. These spongy masses were taken out of the liquid for closer examination and washed in distilled water. It was then found that they had taken up the main part of the arsenic present in the liquid which retained only traces. Whether in this case the arsenic as separated really combines with the tin as tin arsenide, or if the arsenic remains in the spongy tin in a state of fine metallic division, must be left undecided.

In a check experiment the following conditions were observed. As working with the apparatus above described offers the inconvenience that the addition of liquids into the hot round flask through the dropping funnel can be effected only with the utmost caution, in order to avoid a reflux occasioned by the momentary cooling, there was inserted after the round flask, containing now 300 c.c. of materials, a Woulf's bottle, holding 150 c.c., the gas introductory tube of which was provided with a Bunsen valve or a glass ball valve. Thus a reflux was rendered impossible, and it was no longer necessary to observe the working of the apparatus. The Woulf's bottle was now connected with three receivers each of the capacity of 100 c.c.; all contained silver solution 1:50, and the Woulf's bottle as much as corresponded to the arsenic used in the experiment.

The precaution was also employed that all the liquids could be forced into the round flask by a pressure of hydrogen, whereby any ascent of gas bubbles in the dropping flask was at once excluded.

Since the zinc used (not the same as that used in the

* Zeit. Anorganische Chemie.

former experiments, which had all been consumed) was found on careful examination to contain a minimum trace of zinc, this trace was first determined in the apparatus. 30 grms. of the zinc were found to contain 0.00375 per cent of arsenic, corresponding to 0.3 c.c. of the decinormal solution of iodine, which was consumed on titrating the contents of the receivers. If, therefore, again 20 c.c. of the 1 per cent solution of arsenic, which required as before on titration 40.2 c.c. of decinormal solution of iodine, were volatilised in the apparatus as arsenic hydride by means of 30 grms. of zinc, the titration of the contents of the receivers after elimination of the excess of silver, &c., must show an excess of 0.3 c.c. of the standard liquid. This was, in fact, the case. On titration there were consumed 40.47 c.c., consequently there were found 40.17 c.c. of the decinormal solution. Thus the availability of the method was demonstrated.

Further experiments are intended, and the method will be especially tested to find whether it may be ultimately available for a separation of arsenic from antimony, or for the determination of both elements when simultaneously present. Whilst arsenic hydride reacts with a dilute silver solution to form arsenious acid, and to liberate metallic silver, antimony hydride precipitates from a solution of silver, even if its concentration is only 1:80, merely black silver antimonide, upon which behaviour the separation of both elements may possibly be based.

This profound difference in the behaviour of both hydrogen compounds with dilute solutions of silver is also theoretically interesting. If we reflect that in the oxygen compounds of the trivalent elements, N, P, As, Sb, consequently in N_2O_3 , P_2O_3 , As_2O_3 , Sb_2O_3 , the acid character continually decreases, and that with higher atomic weights basic characters become more perceptible, and that in the corresponding hydrogen compounds, NH_3 , PH_3 , AsH_3 , SbH_3 , the behaviour is exactly the reverse, we are inclined to ascribe to antimony hydride faintly acid properties which come clearly into evidence in their action upon dilute silver solutions. For the recognition of antimony hydride as a feeble acid—feebler than sulphuretted hydrogen—we have the testimony of the occurrence in nature of silver antimonide, whilst silver arsenide is known neither chemically nor as a mineral.

The above described method is a simple means for the determination of arsenic, and is the more important in toxicology, as in forensic inquiries arsenic is almost exclusively recognised by the Marsh test.

CORRESPONDENCE.

ESTIMATION OF CAOUTCHOUC.

To the Editor of the Chemical News.

SIR,—I should like to know how your correspondent, Mr. Phillips, estimated the amount of caoutchouc in his analysis of an indiarubber mat, and how he proved conclusively the absence of an indiarubber substitute. I have been connected with the trade some years, and during the whole of my experience I have never seen or heard of a mat being made of 50 per cent pure caoutchouc, —its price would be prohibitive.—I am, &c.,

PERCY CARTER BELL, F.I.C., F.C.S.

34, Poulton Rd., Fleetwood,
August 8, 1892.

New Derivatives of Amethylcamphonitroketone.—P. Cazeneuve.—The author describes the sodium-, the ethyl-, and sodium-ethyl, the acetyl- and sodium-ethyl derivatives.—*Bull. de la Soc. Chim. de Paris*, Series 3, vii.—viii., No. 11.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

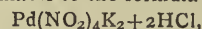
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 2, July 11, 1892.

Determination of the Density of Gases.—Henri Moissan and Henri Gautier.—This paper requires the two accompanying figures.

The Alkoylcyanocamphors and the Benzeneazocamphocarbonic Ethers.—A. Haller.—An account of the benzeneazocamphocarbonic ethers, and especially of the methyl- and ethyl-benzeneazocamphocarbonates.

A Palladium Chloronitrate.—M. Vèzes.—The composition of this compound answers to the formula $Pd(NO_2)_2Cl_2K$. It may be prepared by the limited action of hydrochloric acid upon potassium palladionitrite in proportion conformable to the formula—



or by the limited action of potassium nitrite upon potassium chloropalladite, or by the action of potassium chloropalladite upon potassium palladionitrite in equivalent proportions. It is unalterable in air, and does not lose water at 100°. At dull redness it is decomposed with production of nitrous vapours, leaving a residue of palladium and potassium chloride. It is soluble in about three times its weight of cold water and twice its weight of boiling water.

Double Chlorides formed by Lithium Chloride and Chlorides of the Magnesian Series.—A. Chassevant.—The author has obtained four chlorides formed by combining lithium chloride with manganese, iron, cobalt, and nickel chlorides. These compounds have all a formula corresponding to the formula $2MCl, LiCl, 6H_2O$. They all contain the same quantity of crystalline water. They are all easily dissociable into their elements by water, but stable in presence of an excess of one of their components, lithium chloride. They have the colour of the anhydrous chloride of the metal which enters into their composition. Thus the double chloride of nickel and lithium is yellow, and that of the double chloride of cobalt and nickel is blue. Heat decomposes them, forming either an oxychloride or an oxide of the metal which enters into their composition. They are all efflorescent in a dry atmosphere, and in these conditions lose hydrochloric acid. They are isomorphous.

Researches on Nickel and Cobalt.—Ch. Lepierre and M. Lachaud.—In a former communication the authors describe the action of ammonium bisulphate upon the salts of iron. They now describe the new substances obtained with nickel and cobalt. The series of compounds obtained with nickel and cobalt are analogous to those of iron, though less complete.

On the Quinine Iodomethylates.—E. Grimaux.—Quinine, $C_{20}H_{24}N_2O_2$, may be considered as formed of two groups, one approximating to quinoline, and the other probably of pyridic or piperidic character. It constitutes a diacid base, which may be united to 1 or 2 mols. of monobasic acids, or may combine with 1 mol. or 2 mols. of methyl iodide to form monoiodomethylate or di-iodomethylates. The author, whilst studying the action of alkalis upon iodomethylates in the cold, has determined upon which of the atoms of nitrogen in quinine the first mol. of CH_3I is fixed in the formation of iodomethylates.

On Methylated Camphocarbonic Ethers, Methyl-Camphor, and certain Nitrogen Derivatives of Cyanocamphor.—J. Minguin.—Not suitable for abstraction.

Action of Non-Metallic Nitrides and Hydronitrides upon the Oxyhydrocarbonic Compounds.—R. Vidal.—The author has obtained the naphthol β , a product which represents the same centesimal composition as the dinaphthylamines, but it differs by its physical and chemical characters. It melts only at 225° and does not combine with acids.

Certain Ferruginous Medicines.—H. Le Chatelier.—The author holds that it is practically impossible to find in commerce at Paris so-called chalybeate waters which contain a notable quantity of iron. Certain of these waters contained it regularly twenty years ago.

Contributions to the Study of Mineral Waters; on Alumina contained in Waters.—F. Parmentier.—The authors have found alumina in all natural waters, mineral or others, which they have analysed. They have also found alumina in notable quantities in springs formerly studied, though the published analyses do not mention it.

Respiratory Value of Hæmocyanine.—L. Cuenot.—In blood containing hæmocyanine the blood is capable of absorbing more oxygen than an equal volume of water, but its absorbent power for oxygen is very feeble compared with the hæmoglobine of the vertebrates. The author throws doubts on the experiments of Dr. Griffiths.

Physiological Action of Spermine. Interpretation of its Effects on the Organism.—Alexandre Poehl.—The author assigns to pure spermine the formula $C_5H_{14}N_2$.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Edinburgh Meeting of the British Association:—

President—Professor Herbert McLeod, F.R.S., F.C.S.
Vice-Presidents—Professor A. Crum Brown, M.D., D.Sc., F.R.S., F.R.S.E., Pres. C.S.; J. H. Gladstone, Ph.D., F.R.S.; Professor F. R. Japp, M.A., Ph.D., LL.D., F.R.S., F.C.S.; Professor W. H. Perkin, jun., Ph.D., F.R.S., F.R.S.E., F.C.S.; Professor Otto Pettersson; Professor T. Purdie, Ph.D., B.Sc., F.C.S.; Professor J. Emerson Reynolds, M.D., D.Sc., F.R.S., F.C.S., M.R.I.A.; Professor W. C. Roberts-Austen, C.B., F.R.S., F.C.S.

Secretaries—J. Gibson, Ph.D., F.R.S.E.; H. Forster Morley, M.A., D.Sc., F.C.S. (*Recorder*); D. H. Nagel, M.A., F.C.S.; W. W. J. Nicol, M.A., D.Sc., F.R.S.E., F.I.C.

Committee—J. Y. Buchanan, F.R.S.; Professor Campbell Brown; Professor Clowes; Dr. Colman; W. S. Curphey; William Crookes, F.R.S.; Professor A. E. Dixon; A. E. Fletcher; Professor Hartley, F.R.S.; Dr. C. A. Kohn; Professor Living, F.R.S.; Dr. Stevenson Macadam; Dr. H. Marshall; Professor Meldola, F.R.S.; Professor W. Ramsay, F.R.S.; J. B. Readman; Dr. A. Richardson; W. A. Shenstone; T. Turner; Dr. J. Walker; V. H. Veley.

The Papers brought before the Section were as follows:—

President's Address.

Professor Crum Brown, F.R.S., and Dr. J. Walker.—Electrolytic Synthesis.

Professor W. Ramsay, F.R.S.—Impurities in Chloroform.

Report of the Committee on the Properties of Solutions.

Report of the Committee on the Bibliography of Solutions.

Report of the Committee on Wave-length Spectra of the Elements.

T. W. Hogg.—Some Alloys of Iron, Manganese, and Aluminium.

B. Lean and W. A. Bone.—The Explosion of Ethylene with less than its own volume of Oxygen.

Prof. V. B. Lewes.—Luminosity of Hydrocarbon Flames.

Prof. A. Smithells.—Experiments on Flame.

Report of the Committee on the direct formation of Haloids from Pure Materials.

Dr. J. A. Harker.—The Reaction of Hydrogen with Mixtures of Oxygen and Chlorine.

Prof. W. R. Hodgkinson and Col. Trench.—Action of Dry Ammonia on Sulphates.

Prof. W. R. Hodgkinson and J. Young.—Action of Dry Sulphur Dioxide on Oxy-salts.

Prof. F. Clowes.—The application of a Hydrogen Flame in the Safety Lamp to the Detection and Estimation of Inflammable Gases and Vapours in Air.

Report of the Committee on the Influence of the Silent Discharge of Electricity on Oxygen and other Gases.

Report of the Committee appointed to consider the best Method of Establishing an International Standard for the Analysis of Iron and Steel.

Dr. J. H. Gladstone, F.R.S.—Notes on the Molecular Refraction and Dispersion of (a) Metallic Carbonyls, (b) Indium and Gallium, (c) Sulphur.

Prof. W. C. Roberts-Austen, F.R.S.—The Effect of Small Quantities of Foreign Matter on the Properties of Metals.

Dr. Svante Arrhenius.—Researches on Diffusion.

Prof. W. Ramsay, F.R.S.—The Transpiration of Hydrogen through Palladium.

Dr. G. H. Bailey.—The Impurities of Town Air.

Prof. W. H. Perkin, jun., F.R.S.—Syntheses with the aid of Butane and Pentane Tetra-carboxylic Ethers.

Dr. F. Stanley Kipping.—Synthesis of Hydrindone Derivatives.

Dr. F. Stanley Kipping.—Heptamethylene Derivatives.

Dr. F. Stanley Kipping.—Action of Phosphoric Anhydride on Fatty Acids.

Dr. J. Walker.—Methyl Salts of Camphoric Acid.

Dr. L. Dobbin and Dr. J. Walker.—Halogen Addition Products of Salts of Organic Bases.

J. F. Isaac.—The Production of Acetic Acid from the Carbohydrates.

Dr. W. W. J. Nicol.—The Molecular Volumes of Organic Compounds in Dilute Solution.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on the Action of Light on Dyed Colours.

Dr. Shields.—On the amount of Hydrolysis in Aqueous Solutions of Salts of Strong Bases with Weak Acids.

B. Lean and W. A. Bone.—A new Method of Measuring the Pressure produced in Gaseous Explosions.

Dr. F. E. Matthews.—The Determination of Small Quantities of Nitrogen in Soils.

Dr. J. J. Kyle.—A Vanadiferous Lignite.

G. Carrington Purves.—Sewage Precipitation.

Prof. W. Ramsay, F.R.S., and Emily Aston.—The Atomic Weight of Boron.

Dr. J. Gibson.—Preparation of Pure Glucina and the Atomic Weight of Glucinum.

Dr. J. Gibson.—Note on Exact Weighing.

Dr. J. Gibson.—Analysis of Manganese Nodules.

Prof. W. Ostwald.—On the Assumed Potential Difference between Metals in the Solid and in the Molten State.

Prof. H. McLeod, F.R.S.—Iodides of Sulphur.

Dr. W. W. J. Nicol.—Solutions of Iodine.

Dr. H. Marshall.—Persulphates.

Dr. H. Marshall.—Cobaltic Salts.

Report of the Committee on the Bibliography of Spectroscopy.

Report of the Committee on the Action of Light on the Hydracids of the Halogens in presence of Oxygen.
Report of the Committee on the Proximate Constituents of Coal.

W. Durham.—Note on Valency and Atomicity.
Thos. Ewan and W. R. Ormandy.—On a Method for Determining the Vapour Pressures of Solutions.

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Full particulars of this COURSE, qualifying for the VICTORIA UNIVERSITY DEGREES in CHEMISTRY and the COLLEGE TECHNOLOGICAL CHEMISTRY CERTIFICATE, will be forwarded on Application. The Session commences October 4th.

H. W. HOLDER, M.A.,
Registrar.

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(With Queen's Faculty of Medicine).

PRINCIPAL—PROF. R. S. HEATH, M.A., D.Sc.

Faculties of Arts and Science.

The SESSION 1892-93 will be opened on FRIDAY, SEPTEMBER 30, 1892, by Prof. SIR GEORGE HUMPHRY, M.D., F.R.S., F.R.C.S., who will distribute the Prizes and deliver an ADDRESS.

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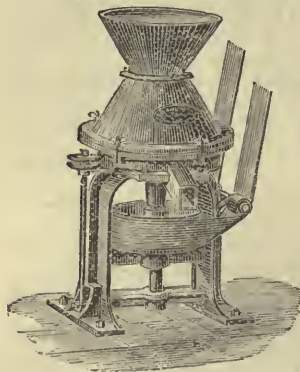
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ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION, EDINBURGH, 1892.

By Prof. ARTHUR SCHUSTER, Ph.D., F.R.S., F.R.A.S.,
President of the Section.

(Concluded from p. 81).

ONE of the principal obstacles to the rapid diffusion of a new idea lies in the difficulty of finding suitable expressions to convey its essential point to other minds. Words may have to be strained into a new sense, and scientific controversies constantly resolve themselves into differences about the meaning of words. On the other hand, a happy nomenclature has sometimes been more powerful than rigorous logic in allowing a new train of thought to be quickly and generally accepted.

A good example is furnished by the history of the science of energy. The principle of the conservation of energy has undoubtedly gained a more rapid and general acceptance than it would otherwise have had by the introduction of the word potential energy. A great theorem, which in itself seems to me to be an intricate one, has been simplified by calling something energy which, in the first place, is only a deficiency of kinetic energy. The only record I can find on the history of the expression is given in Tait's "Thermodynamics," wherein the term statical energy is ascribed to Lord Kelvin, and that of potential energy to Rankine. It would be of interest to have a more detailed account on the origin of an expression which has undoubtedly had a marked influence not only on the physics, but also on the metaphysics of our time. But while fully recognising the very great advantage we have derived from this term "Potential Energy," we ought not, at the same time, to lose sight of the fact that it implies something more than can be said to be proved. It is easy to overstep the legitimate use of the word. Thus, when Professor Lodge (*Phil. Mag.*, xi., p. 36, 1881) attempts to prove that action at a distance is not consistent with the doctrine of energy, he cannot, in my opinion, justify his position except by assuming that all energy is ultimately kinetic. That is a plausible, but by no means a necessary theory. Efforts have been made to look on energy as on something which can be labelled and identified through its various transformations. Thus we may feel a certain bit of energy radiating from a coal fire, and if our knowledge was complete, we ought to be able to fix the time at which that identical bit of energy left the sun and arrived on the surface of the earth, setting up a chemical action in the leaves of the plant from which the coal has been derived. If we push this view to a logical conclusion, it seems to me that we must finally arrive at an atomic conception of energy which some may consider an absurdity.

Let, for instance, a number of particles P_1 , P_2 , &c., in succession, strike another particle Q . How can we in the translatory energy of the latter identify the parts which P_1 , P_2 , &c., have contributed? According to Professor Lodge's view, we should be able to do so, for if the particle Q in its turn gives up its energy to others, say R_1 , R_2 , R_3 , &c., we ought to be able to say whether the energy of P_1 has ultimately gone into R_1 or into R_2 , or is divided between them. It is only by imagining that all energy is made up of a finite number of bits, which

pass from one body to another, that we can defend the idea of considering energy as capable of being "labelled."

In the expressions we adopt to describe physical phenomena we necessarily hover between two extremes. We either have to choose a word which implies more than we can prove, or we have to use vague and general terms which hide the essential point, instead of bringing it out. The history of electrical theories furnishes a good example. The terms positive and negative electricity committed us to something definite; we could reckon about quantities of electricity, and form some definite notion of electrical currents as a motion of the two kinds of electricity in opposite directions. Now we have changed all that; we speak of electric displacements, but safeguard ourselves by saying that a displacement only means a vector quantity, and not necessarily an actual displacement. We speak of lines and tubes of force not only as a help to realise more clearly certain analytical results, but as implying a physical theory to which, at the same time, we do not wish to commit ourselves. I do not find any fault with this, for it is a perfectly legitimate and necessary process to state the known connection between physical phenomena in some form which introduces the smallest number of assumptions. But the great question "What is electricity?" is not touched by these general considerations. The brilliant success with which Maxwell's investigations have been crowned is apt to make us overrate the progress made in the solution of that question. Maxwell and his followers have proved the important fact that optical and electrical actions are transmitted through the same medium. We may be said to have arrived in the subject of electricity at the stage at which optics was placed before Young and Fresnel hit on the idea of transverse vibrations, but there is no theory of electricity in the sense in which there is an elastic solid theory of light.

If the term electrical displacement was taken in its literal sense, it would mean that the electric current consists of the motion of the ether through the conductor. This is a plausible hypothesis, and one respecting which we may obtain experimental evidence. The experiments of Rayleigh and others have shown that the velocity of light in an electrolyte, through which an electric current is passing, is, within experimental limits, the same with and against the current. This result shows that if an electrical current means a motion of the ether the velocity of the medium cannot exceed ten metres a second for a current density of one ampère per square centimetre. This, then, is the upper limit for a possible velocity of the medium; can we find a lower limit? The answer to that question depends on the interpretation of a well-known experiment of Fizeau's, who found that the speed of light is increased if it travels through water which moves in the same direction as the light. If this experiment implies that the water carries the ether with it, and if a motion of the ether means an electric current, we should be led to the conclusion that a current of water should deflect a magnet in its neighbourhood. An experiment made to that effect would almost certainly give a negative result, and would give us a lower limit for the velocity of the medium corresponding to a given current. Such an experiment, together with that of Rayleigh, would probably dispose of the theory that an electric current is due to a translatory velocity of the medium. This would be an important step, and it would be worth while to arrive at a final settlement of the question.* The whole question of the relation between the motion of matter and the motion of the medium is a vital one, and we shall probably not make any serious advances until experiment

* Fizeau's result must either be due to the motion of matter through the medium or to the fact that moving matter carries the ether with it. If it is due to the former cause, and matter does not carry the ether with it, may we not consider that matter moving through the ether, that is a relative motion of matter and ether, must produce effects equal and opposite to those of ether moving through matter? In that case the reasoning in the text would, *mutatis mutandis*, hold good.

has found a new opening. But we must expect many negative results before some clue is discovered. Nor can we attach much importance to negative results unless they are made by someone in whose care and judgment we place full reliance. We should all the more, therefore, recognise the courage and perseverance of those who spend their valuable time in such investigations as Professor Lodge has recently undertaken. That ultimately some relation will be found between moving matter and electrical action there is no reasonable doubt.

One of the most hopeful openings for new investigations has always been found in the pursuing of a theory to its logical conclusions, and there is one result of the electromagnetic theory of light which has not, in my opinion, received the share of attention which it deserves.

When sound passes through air it is propagated more quickly with the wind than against it, and we may easily find the velocity relative to the earth by combining the ordinary sound velocity with the velocity of the wind. Similarly, when any waves pass through a medium moving with uniform velocity, the waves being due to internal stresses in the medium, we may treat of the velocity of the waves independently of that of the medium, and say that the wave-velocity in the direction of motion of the medium, and relative to a fixed body, is the sum of the wave-velocity calculated on the supposition that the medium is at rest and the velocity of the medium. Professor J. J. Thomson (*Phil. Mag.*, vol. ix., p. 284, 1880), applying Maxwell's equations, has arrived at a different result for electromagnetic waves, and has come to the conclusion that in order to get the velocity of light along a stream of flowing water, we have to add to the velocity of light only half the velocity of water. The following considerations suggest themselves to me with respect to this result. Maxwell's theory is founded on certain observed effects, which all depend on the relative motion of matter. A result such as the one referred to implies actions depending on absolute motion, and appears therefore to point to something which has been introduced into the equations for which there is no experimental evidence. The only assumption clearly put down by Maxwell is that electromagnetic actions are transmitted through the medium, and it is possible that that assumption necessarily carries Prof. J. J. Thomson's result with it. If a careful examination of the subject should show that this is the case, we are brought face to face with a serious difficulty. It is said, with justice, to be one of the great advantages of Maxwell's theory that it does away with action at a distance; but what do we gain if we replace action at a distance by something infinitely more difficult to conceive, namely, internal stresses of a medium depending on the velocity of the medium through space? I can only see one loophole through which to escape, namely, that Maxwell's medium is not homogeneous, but consists of two parts, and that if we speak of the medium as moving, we mean the motion of one of these parts relative to the other.

While we may hope to obtain important results from an investigation of the relation between what we call electricity and the medium, we must not lose sight of another avenue, namely, the relation between electricity and chemical effects. The passage of electricity through gases presents us with a complicated problem to which a number of physicists have given their attention of late years. There seems no reasonable doubt that electricity in a gas is conveyed by the diffusion of particles conveying high charges, probably identical with those carried by the electrolytic ion. The fact that this convection is a process of diffusion with comparatively small velocity is shown by the experimental result that the path of the discharge is affected by any bodily motion of the gas which conveys the current. Even the convection currents due to the heat produced by the discharge itself are sufficient to deflect the luminous column which marks the passage of the current.

The most puzzling fact, however, connected with the

discharge of electricity through gases consists in the absence of symmetry at the positive and negative poles. There must be some difference between a positively and negatively charged atom which seems of fundamental importance in the relation between matter and what we call electricity. A discussion of the various phenomena attending the discharge of electricity through gases seems to me to point to a conclusion which may possibly prove a step in the right direction.

A surface of separation between bodies having different conductivities becomes electrified by the passage of a current, while at the surface between two chemically distinct bodies we have, according to Helmholtz, a sheet covered at the two sides with opposite electricities. These surface electrifications are not merely imaginary layers invented to satisfy mathematical surface conditions. They can be proved to be realities. Thus, when one electrolyte floats on another, the specific resistances being different, we often observe secondary chemical effects due to the action of the ions which carry the surface electrification.

If the passage of electricity from the solid to the gas involves some work done, we must expect a double sheet of electricity at the boundary, the gas in contact with the kathode becoming positively, and that in contact with the anode negatively, electrified. *A priori* we can form no idea how a layer of gas, the atoms of which carry charges, will behave. The ordinary proof that all electrification must be confined to the surface implies that all forces act according to the law of the inverse square, but where we have also to consider molecular forces, I see no reason why the electrification at a surface may not stretch across a layer having a thickness comparable with the mean free path of the molecule. It is here that there seems to be the fundamental difference between positive and negative electricity. A negative electrification of the gas, like that of a solid or a liquid, seems always confined to the surface, and no one has ever observed a volume electrification of negative electricity. The case is different for the positively electrified part of the gas. Wherever from other considerations we should expect a positively electrified surface sheet, we always get a layer of finite thickness. The result implies a different law of impact between positively and negatively electrified ions, but I see no inherent improbability in this. That the kathode jet into a gas is surrounded by a positively electrified layer of finite thickness extending outwards must be considered as an established fact, and several of the characteristic features of the discharge are explained by it. The large fall of potential at the kathode can also be explained on the view which I have put forward, for in order to keep up the discharge there must be a sufficient normal force at the surface, and if this force is not confined to the surface, but necessarily stretches across a finite layer, the fall of potential must be multiplied a great number of times. Similarly Goldstein has shown that some of the phenomena of the kathode are observed at every place at which the positive current flows from a wide to a narrow part of a column of gas. At such places we should expect a positive surface electrification, and here, again, the whole appearance tends to show that we are dealing with a positive volume electrification. No corresponding phenomena are observed when the current passes from the narrow to the wide part.

The fact that in all cases experimented upon positive volume electrifications are observed, but never similar negative electrifications, is surely of significance.

Some of the results recently brought to light by investigations on the discharge of electricity have interesting cosmical applications. Thus it is found that such a discharge through any part of a vessel containing a gas converts the whole gas into a conductor.* The dissociation

* An experiment by Hittorf (*Wied. Ann.*, vii., p. 614), suggested the probability of this fact, which was proved independently by Arrhenius and myself.

tion which we imagine to take place in a liquid before electrolytic conduction takes place must be artificially produced in a gas by the discharge itself. We may imitate in gases which have thus been rendered conductive many of the phenomena hitherto restricted to liquids; thus I hope to bring to the notice of this meeting cases of primary and secondary cells in which the electrolyte is a gas. There are other ways in which a gas can be put into that sensitive state in which we may treat it as a conductor, and we have every reason to suppose that the upper regions of our atmosphere are in this state. The principal part of the daily variation of the magnetic needle is due to causes lying outside the surface of the earth, and is in all probability only an electro-magnetic effect due to that bodily motion in our atmosphere which shows itself in the diurnal changes of the barometer. A favourite idea of the late Prof. Balfour Stewart will thus probably be confirmed. The difference in the diurnal range between times of maximum and times of minimum sun-spots is accounted for by the fact that the atmosphere is a better conductor at times of maximum sun-spots.

The mention of sun-spots raises a point not altogether new to this section. Careful observations of celestial phenomena may suggest to us the solution of many mysteries which are now puzzling us. Consider, for instance, how long it would have taken to prove the universal property of gravitational attraction if the record of planetary motion had not come to the philosopher's help. And surely the most casual observation of cosmical effects teaches us how much we have yet to learn.

The statement of a problem occasionally helps to clear it up, and I may be allowed, therefore, to put before you some questions, the solution of which seems not beyond the reach of our powers.

1. Is every large rotating mass a magnet? If it is, the sun must be a powerful magnet. The comets' tails, which eclipse observations show stretching out from our sun in all directions, probably consist of electric discharges. The effect of a magnet on the discharge is known, and careful investigations of the streamers of the solar corona ought to give an answer to the question which I have put.*

2. Is there sufficient matter in interplanetary space to make it a conductor of electricity? I believe the evidence to be in favour of that view. But the conductivity can only be small, for otherwise the earth would gradually set itself to revolve about its magnetic pole. Suppose the electric resistance of interplanetary space to be so great that no appreciable change in the earth's axis of rotation could have taken place within historical times, is it not possible that the currents induced in planetary space by the earth's revolution may, by their electromagnetism, cause the secular variation of terrestrial magnetism? There seems to me to be here a definite question capable of a definite answer, and as far as I can judge, without a strict mathematical investigation, the answer is in the affirmative.

3. What is a sun-spot? It is, I believe, generally assumed that it is analogous to one of our cyclones. The general appearance of a sun-spot does not show any marked cyclonic motion, though what we see is really determined by the distribution of temperature and not by the lines of flow. But a number of cyclones clustering together like the sun-spots in a group should move round each other in a definite way, and it seems to me that the close study of the relative positions of a group of spots should give decisive evidence for or against the cyclone theory.

4. If the spot is not due to cyclonic motion, is it not possible that electric discharges setting out from the sun,

and accelerating artificially evaporation at the sun's surface, might cool those parts from which the discharge starts and thus produce a sun-spot? The effects of electric discharges on matters of solar physics have already been discussed by Dr. Huggins.

5. May not the periodicity of sun-spots, and the connection between two such dissimilar phenomena as spots on the sun and magnetic disturbances on the earth, be due to a periodically recurring increase in the electric conductivity of the parts of space surrounding the sun? Such an increase of conductivity might be produced by meteoric matter circulating round the sun.

6. What causes the anomalous law of rotation of the solar photosphere? It has long been known that groups of spots at the solar equator perform their revolution in a shorter time than those in a higher latitude; but spots are disturbances which may have their own proper motions. Duner* has shown, however, from the displacement of the Fraunhofer lines, that the whole of the layer which produces these lines follows the same anomalous law, the angular velocity at a latitude of 75° being 30 per cent less than near the equator.† As all causes acting within the sun might cause the angular velocity of the sun to be smaller at the equator than at other latitudes, but could not make it greater, the only explanation open to us is an outside effect either by an influx of meteoric matter, as suggested by Lord Kelvin, or in some other way. If we are to trust Dr. Welsing's result, that faculae which have their seat below the photosphere revolve in all latitudes with the same velocity, which is that of the spot velocity in the equatorial region, we should have to find a cause for a retardation in higher latitudes rather than for an acceleration at the equator. The exceptional behaviour of the solar surface seems to me to deserve very careful attention from solar physicists. Its explanation will probably carry with it that of many other phenomena.

In conclusion, I should like to return for an instant to the question whether it is possible by any means to render the progress of science more smooth and swift. If there is any truth in the idea that two types of mind are necessary, the one corresponding to the boiler and the other to the cooler of a steam engine, it must also be true that some place must be found where the two may bring their influence to bear on each other. I venture to think that no better ground can be chosen than that supplied by our meetings. We hear it said that the British Association has fulfilled its object; we are told that it was originally founded to create a general interest in scientific problems in the towns in which it meets; and now that popular lectures and popular literature are supposed to perform that work more satisfactorily, we are politely asked to commit the happy despatch. There is no need to go back to the original intention of those who have founded this institution, which has at any rate adapted itself sufficiently well to the altered circumstances to maintain a beneficial influence in scientific research.

The free discussion which takes place in our sections, the interchange of ideas between men who during the rest of the year have occupied their minds, perhaps too much, with some special problem, the personal intercourse between those who are beginning their work with sanguine expectations, and those who have lost the first freshness of their enthusiasm, should surely one and all ensure a long prosperity to our meetings. If we cannot claim any longer to sow the seeds of scientific interest in the towns we visit, because the interest is established, we can at any rate assure those who so kindly offer us hospitality, that they are helping powerfully in the promotion of the great object which we all have at heart.

* "Oefvers. af Kongl. Vetensk. Ak. Forhandl.," p. 47, 1890.

† Although the importance of M. Duner's results would make an independent investigation desirable, the measurements of Mr. Crew, who by a much inferior method arrived at other results, cannot have much weight as compared with those of Duner.

* The efforts of Mr. Bigelow have a bearing on this point, also some remarks which I have made in a lecture before the Royal Institution (*Proc. Roy. Inst.*, 1891), but nothing decisive can be asserted at present.

VOLUMETRIC DETERMINATION OF
MERCURY.

By ROD. NAMIAS.

THE volumetric process to be explained is applicable only to mercuric chloride, into which every other compound must be previously converted. The nitrate must be treated with hydrochloric acid in excess, and evaporated to dryness; the mercurous salts are submitted to evaporation in presence of hydrochloric acid and of potassium chlorate.

The evaporation must be conducted with care at a temperature below that of ebullition, so as to avoid any loss of mercuric chloride by volatilisation.

The process depends upon the following principle:—If to a solution of mercuric chloride, slightly acidified with hydrochloric acid, we add a solution of stannous chloride, the mercuric chloride is reduced first to the mercurous state and then to metallic mercury. But whilst the first reaction is nearly instantaneous, the second takes a longer or shorter time, so much the longer as the excess of the stannous chloride is less.

If we have a reagent by which we can recognise the moment when the stannous chloride is in excess for the first reaction, and begins to produce the second, we may by this means determine the mercury volumetrically.

The reagent for detecting the presence of stannous chloride in excess is sodium molybdate. I dissolve a small quantity of molybdic anhydride in a solution of sodium hydrate or carbonate; I steep in this liquid a morsel of filter-paper, which I spread out whilst wet upon a plate of porcelain. The solution of molybdate ought to be freshly prepared, and the paper of good quality; it must not take a yellow tint on immersion in the alkaline liquid. The paper must be steeped in the molybdate only a little time before the experiment, so that it may not have time to dry.

The paper thus prepared shows a relatively slight excess of stannous chloride, which communicates to it according to its quantity a colour varying from the lightest sky-blue to an intense blue. This colour is due to the reduction of the molybdic acid. Ammonium molybdate, less stable than sodium molybdate, is less fit for use.

The determination of the value of the stannous solution may be made by means of a standard solution of iodine; but it is preferably effected by operating upon a known quantity of pure mercuric chloride obtained by sublimation.

If we operate with iodine we obtain a slight error in excess due to the small quantity of stannous chloride, which must be used in excess to mark the end of the operation by spotting upon the molybdate paper. In any case it is well to determine the standard of the stannous solution by means of iodine approximately, if not exactly; this serves as a control, and facilitates at the same time the exact titration by means of mercuric chloride.

To prepare the solution of stannous chloride I dissolve 2 to 3 grms. tin by means of hydrochloric acid, and dilute it to 1 litre. This solution is preserved in an apparatus which prevents alteration by contact with air. I determine its strength as follows:—0.2 to 0.4 grm. of mercuric chloride weighed exactly are dissolved in 50 c.c. of distilled water, and acidulated with $\frac{1}{2}$ c.c. of concentrated hydrochloric acid. Into this cold solution the stannous solution is allowed to flow from a burette. If the determination of the standard has been previously made with iodine, we may pour in at once, without fear of overstepping the limit, the volume as determined by calculation from the titration with iodine; we then add the liquid drop by drop, stirring carefully, and each time putting a drop of the mixture with the stirring-rod upon the molybdate paper. An excess of a few drops of the stannous liquid turns the paper to a pale blue, which be-

comes manifest after a few seconds, and which an experienced eye easily recognises.

To obtain a well-marked colouration, it is necessary to use an excess of from 0.3 to 0.5 c.c. for 50 c.c. of liquid. The small quantity of mercurous chloride placed upon the molybdate paper whilst "spotting" has no injurious influence upon the result.

The proportion of free hydrochloric acid contained in the liquid should be about 0.5 c.c. to 50 c.c. of the liquid; a larger proportion may occasion errors from its action upon the molybdic acid in presence of filter-paper.

To obtain exact results we must operate each time exactly as when standardising the liquid. We must, as far as possible, operate upon the same volume of liquid, in presence of the same proportion of hydrochloric acid, and obtain spots of the same intensity upon the molybdate paper.—*Revue Universelle des Mines.*

ANALYSIS OF COPAL RESINS.

By ED. KRESSEL.

Of all copals Zanzibar copal is the only one entirely free from taste and aroma; all other kinds possess more or less aroma, and some of these (Borneo and Manilla copal) a bitter aromatic taste. According to Brisson the specific gravity varies from 1.045 to 1.139, but in these estimations the air enclosed in the copal has not been regarded. The melting-point of a copal resin depends upon the hardness; the harder the resin the higher the melting-point. Andés gives the following average scale for hardness, which I have found to be correct:—

"Zanzibar, Sierra Leone, Angola, Benguela, Accra, Benin, Loango, Kauri, Manilla, Borneo, Singapore."

A good, hard, nearly colourless copal dried for some time over H_2SO_4 gave:—

	I.	II.	Average.
C	78.87	79.37	79.12
H	9.95	10.18	10.065
O	11.18	10.45	10.815
	100.00	100.00	100.00

With benzol, chloroform, disulphide of carbon, or ether, the powdered resin swells considerably; on putting to rest, a gelatinous mass will separate from the solution, which remains clear on top. I used freshly distilled ether entirely free of water as a solvent. I repeated the extraction of the resin with ether, until a few drops left little or no residue on evaporation. The substance insoluble in ether requires some considerable time to dry and to become of constant weight, and when so, it appears like horn. It is called "swell copal," as it only swells in every solvent and does not go into a clear solution. I found the amount of swell copal to be in proportion to the hardness of the raw copal resin. The copal now in question contained about 64.5 per cent of swell copal. Owing to the nature of this substance, copal resins cannot be used for varnishes in their raw state, but on heating it to a high temperature it is converted into pyro swell copal, which is easily soluble in any solvent.

The analysis of swell copal gave:—

	I.	II.	Average.
C	78.63	79.85	79.24
H	11.29	10.75	11.02
O	10.08	9.40	9.74
	100.00	100.00	100.00

The ether extraction of the raw copal leaves on distilling off the ether a light yellow resin, which is soft and remains so when even subjected to 100° C. for some time. On distillation, an oil goes over at about 132° C., leaving a brown brittle resin.

(To be continued).

* Read before the British Association, Edinburgh Meeting, 1892, Section B

the hydrogen flame enables the miner to detect readily and with certainty percentages of firedamp, varying between 0.25 and 3.0, and to measure their amount. As soon as the delicate testing is finished the ordinary flame of the lamp is kindled, and can be employed either for illumination, or, if lowered, it can be applied to the detection of percentages of gas larger in amount than those found by the hydrogen flame. The hydrogen gas is carried in a small steel reservoir, slung over the shoulder by a strap, and is introduced through a fine metal tube which passes into the interior of the safety-lamp and terminates near the wick. This composite lamp is at once a good illuminator and an extremely delicate gas tester.

Comparative experiments were made with a hydrogen flame, an alcohol flame of the same height, and a small blue benzoline flame, all of which were exposed in air containing 1 per cent of coal-gas. The "cap" seen over the hydrogen flame was nearly four times as high as that seen over the benzoline flame, and half as high again as that seen over the alcohol flame.

Many serious accidents have arisen from bringing a "naked flame" into spaces in which light petroleum oil has been stored. The vapour of this oil, when mingled with the air in proper proportions, is violently explosive; and it becomes important therefore to have means of detecting its presence and measuring its amount. The author described tests carried out with the above hydrogen safety-lamp in his test chamber. They prove that the hydrogen flame can detect one-twentieth of the amount of petroleum vapour which can be kindled in air, and one thirty-sixth of the amount which explodes when mingled with air.

Mr. Vernon Harcourt, Mr. Thomas, of Cardiff, and Profs. Barrett and Smithells, took part in the discussion of the paper, and elicited the following further facts from the author of the paper. The proportion of inflammable gas in air is measured not only by taking the height of the cap but also by noting its appearance, which changes considerably as the percentage of "gas" rises. Further, that the size of the cap produced by a given percentage of gas is increased by the increased temperature and size of the flame. Since air containing less than 1 per cent of this gas is explosive if mixed with coal-dust, it becomes necessary to have a delicate test for gas to ensure the safety of dust mines.

THE EXPLOSION OF ETHYLENE WITH LESS THAN ITS OWN VOLUME OF OXYGEN.*

By B. LEAN, B.A., B.Sc., Dalton Chemical Scholar of
Owen's College, and
W. A. BONE, B.Sc., Fellow of Victoria University.

OUR investigation arose out of experiments to determine the rate of explosion of hydrocarbons with defect of oxygen, and were made at the suggestion of Professor H. B. Dixon. We found that on exploding ethylene with less than its own volume of oxygen, there was invariably a considerable increase in pressure. In case of a mixture of 100 volumes ethylene to 96.5 volumes oxygen, the pressure increased from 756 m.m. to 1503 m.m. of mercury, indicating that the oxygen had mainly gone to the carbon and not to the hydrogen. On carefully analysing the products of explosion we found that, in addition to hydrogen, carbon monoxide, and small percentages of carbonic acid and unsaturated hydrocarbons, there was always present a small amount of some saturated hydrocarbon, presumably marsh gas.

We made and fired five different mixtures of ethylene and oxygen, containing 100 volumes ethylene to from 70 to 96.5 volumes oxygen. We invariably found both

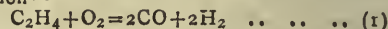
saturated and unsaturated hydrocarbons present in the products of the explosion, and the percentages of both these increased as the percentage of oxygen in the original mixture decreased, as one would naturally expect.

The quantity of marsh gas present in the products of explosion of 100 volumes of ethylene to 70 volumes of oxygen was 5.53 per cent, and in the case of the mixture containing 100 volumes ethylene to 96.5 volumes of oxygen, we found 1.01 per cent of marsh gas in the products.

With regard to the unsaturated hydrocarbons present in the products, a qualitative examination revealed the presence of acetylene. Whether this constitutes the whole of the unsaturated hydrocarbons present we are not prepared to say; it is certainly present in not inconsiderable quantities.

We may be allowed to add a note as to the nature of the reaction when ethylene is exploded with less than its own volume of oxygen.

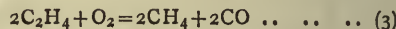
The first reaction which doubtless occurs is a combination between the oxygen and part of the ethylene with the formation of carbon monoxide and hydrogen, according to the equation—



The heat liberated by this reaction produces a decomposition of some of the unburnt ethylene analogous to the decomposition which ethylene undergoes when passed through a red-hot tube into marsh gas and carbon, according to the equation—



Marsh gas might also be produced in another way, by partial oxidation and decomposition, according to the equation—



With regard to the formation of acetylene, this is most probably due to a secondary reaction between the nascent hydrogen formed according to equation (1), and the deposited carbon according to equation (2)—



The value of our experiments lies largely in the fact that as a result of the extremely short period during which the reaction lasts in the explosion coil, the gaseous products must be, in the main, those produced by the original primary reaction, for the rapid cooling of the gases retards the progress of any complicating secondary reaction.

Our investigations have an important bearing upon the question of the luminosity of hydrocarbon flames. The view that the separated carbon, which doubtless is a cause of luminosity, is due to the fact that oxygen combines with hydrogen in preference to carbon can no longer be held. Our work shows that oxygen combines with the carbon in preference to the hydrogen; and in the case of an ethylene flame separated carbon is probably due to the decomposition of ethylene into marsh gas and carbon at high temperatures.

In conclusion we beg to thank Prof. Dixon for many valuable suggestions and kindly oversight of our work.

ATOMIC WEIGHT OF BORON.*

By W. RAMSAY, Ph.D., F.R.S. and EMILY ASTON,
B.Sc. (Lond.).

WE have made a re-determination of the atomic weight of boron by the following methods:—

1. A preliminary re-determination of the water of crystallisation in borax.

2. Conversion of anhydrous sodium borate into sodium chloride by distillation of the borax with hydrochloric acid and methyl alcohol, and weighing the resulting sodium chloride.

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

TABLE I.

Expt. No.	Weight of crystalline borax.	Weight of fused borax.	Percentage of water lost.	Atomic weight of boron.
3	10'3581602	5'4784357	47'1099	11'04
5	5'3440080	2'8246677	47'1433	10'97
6	4'9962580	2'6378934	47'2026	10'85
7	5'7000256	3'0101127	47'1912	10'87
9	5'3142725	2'8065646	47'1882	10'88
11	4'9971924	2'6392016	47'1865	10'885
12	5'2366921	2'7674672	47'1524	10'955
Aggregate ..	41'9466088	22'1631808	47'1633	10'93

Mean atomic weight B=10'921.

Probable error $\pm 0'010$.

TABLE II.

Expt. No.	Weight of fused borax.	Weight of sodium chloride.	Atomic weight of boron.
14	4'7684431	2'7597665	11'015
15	5'2740315	3'0578213	10'925
16	3'2344088	1'8727203	10'992
17	4'0861923	2'3713122	10'879
18	3'4970297	2'0265645	10'949
Aggregate ..	20'8601057	12'0881848	10'951

Mean atomic weight B=10'952.

Probable error $\pm 0'010$.

TABLE III.

Expt. No.	Weight of fused borax $\text{Na}_2\text{B}_4\text{O}_7$.	Weight of sodium chloride NaCl.	Atomic weight of boron.	Weight of silver chloride AgCl.	Chlorine p.c. in sodium chloride.	Atomic weight of boron from chlorine.
22	5'3118075	3'0761181	10'983	7'525869	60'493	11'071
23	4'7805583	2'7700458	10'955	6'7794186	60'515	11'024
24	4'9907395	2'8929844	10'936	7'0804317	60'516	11'003
25	4'7231225	2'7360411	10'968	6'6960242	60'514	11'039
26	3'3137921	1'9187258	10'972	4'6931271	60'479	11'091
Aggregate ..	23'1200199	13'3939152	10'965	32'7748706	60'505	11'084

Mean atomic weight of boron 10'966.
Probable error $\pm 0'005$.Mean atomic weight of boron 11'052.
Probable error $\pm 0'010$.

Pure borax was prepared from pure boracic acid and pure soda. It was found to be an efflorescent substance, so the estimation of the water of crystallisation is hardly a method suited for an atomic weight determination. We made our experiments upon it during damp weather, so that the loss of water that it underwent was not great.

Method I.

Determination of the water of crystallisation in borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

A weighed quantity of borax, generally about 5 grms., was placed in a platinum dish, and heated in an air-bath at a temperature of about 90° — 110° C. for some time; the temperature was gradually raised to about 350° C.; the borax swelled up very much, and in some cases there was loss by spurting; the dish was then taken out of the air-bath, and the borax fused over the blow-pipe; it was then allowed to cool in a desiccator, and the fused borax weighed. The loss in weight gave the percentage of water, from which the atomic weight was calculated.

The results are given in Table I. The mean atomic weight obtained is 10'921 for boron.

The atomic weights used in the calculations are:— $\text{H}=1'008$; $\text{O}=16$; $\text{Na}=23'05$; $\text{Cl}=35'45$; $\text{Ag}=107'92$.

Method II.

Distillation with methyl alcohol and hydrochloric acid.

A weighed quantity of anhydrous borax was dissolved in a small quantity of water, alcohol added, and an excess of pure hydrochloric acid; it was then distilled on a water-bath with addition of methyl alcohol, till boracic acid could no longer be detected in the distillate by the flame test. The flask was then dried in an air-bath at a temperature of about 100° — 110° C. in a slow current of air. The temperature was then raised to about 350° for two or three hours to drive off the last traces of water; the flask was then left to cool, and weighed after it had stood for some time in the balance case.

The weight of salt obtained from the borax was thus determined; the sodium present was calculated; from this number the amount of borax corresponding to two atomic proportions of sodium was found; this number, less Na_2O_7 , gave B_4 , and hence the atomic weight of boron.

In the first series of experiments a flask of soft glass was used. The results obtained were not very concordant, for the glass was attacked, replacement of oxygen by chlorine took place, resulting in the formation of silica and sodium chloride from sodium silicate, for on dissolving the salt in water an insoluble residue of silica was left.

The results are given in Table II.; the mean atomic weight is 10'952, and is not far from that obtained in the next series of distillations.

Second Series.

To avoid the error introduced by the action of the hydrochloric acid and alcohol upon the soft glass, a flask made of combustion tubing was used. It was found that this glass was hardly acted upon, but when the salt was dissolved in water a very slight residue of silica was left. In order to check the results, the chlorine in the sodium chloride was estimated with silver nitrate in the usual manner; the silver chloride was collected on a Gooch's filter, and dried in an air-bath at a temperature of about 200° C. The results obtained gave a rather low percentage of chlorine; calculated with Clarke's atomic weights it is 60'598. If the atomic weight of boron is determined from the chlorine, it is rather higher than that given from the weight of salt.

Since no special precautions were taken to obtain pure silver for the chlorine determinations, but ordinary silver nitrate was employed, it is probable that the distillation results yield the more correct atomic weight of boron, which is therefore 10'966.

METHODS OF SUGAR ANALYSIS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION
OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

(Concluded from p. 73).

PLAN B.—Official Instructions for the Examination of
Chocolates, Candies, and Liquors for the Quantity of
Sucrose contained therein.A.—THE examination, especially of chocolates, preserved
fruits, and liquors, must be primarily directed toward the
detection of starch sugar or honey.B.—The Soleil-Ventzke saccharimeter is used in the
sucrose determinations. The directions for the use of the
instrument will be found in Plan C of the Official Bulletin
published as an appendix to the sugar tariff law of July 9,
1887.Ventzke's scale is so arranged that a 200 m.m. tube
filled with a sugar solution containing 26.048 grms. per
100 c.c. will read 100.If 26.048 grms. of a substance are weighed out, dis-
solved in 100 c.c. of water, and polarised in a 200 m.m.
tube, the number of degrees read on the scale will be the
per cent by weight of sugar in the material.The same is the case when 13.024 grms. are dissolved
in 50 c.c. If this weight (one-half normal weight) has
been dissolved in 100 c.c. the reading of the polariscope
must be doubled.If any other quantity (p grms.) was weighed out, dis-
solved in 100 c.c., and polarised in the 200 m.m. tube, the
number of degrees read on the scale (a) $\times 0.26048$ will
give the grms. sucrose in 100 c.c. of the solution, and—

$$\frac{26.048 a}{p}$$

will give the per cent sucrose in the substance analysed.

In all cases where the substance to be examined con-
tains no other optically active bodies, the direct polarisa-
tion will give accurate results. If such are present, as, for
instance, glucose, invert sugar, maltose, dextrin, pectinous
bodies, the application of the polariscope becomes uncer-
tain, and only in a few cases, which will be given below,
can somewhat reliable results be obtained.As regards the preparation of the solutions the following
must be remembered:—Material which consists mostly
of sucrose and leaves only a small residue on being
treated with water, can be weighed out in the dish,
and the solution immediately transferred to the sugar
flask. When the substance, however, contains much in-
soluble matter, the latter should not be washed into the
flask, as the volume of the sugar solution in such a case
would be less than 100 c.c. In this case the residue must
be separated from the solution by filtration and washing.
Generally the sugar solution is not quite transparent, and
must be treated with some clearing agent. The solutions
serving this purpose are:—

1. Lead acetate, of which from 1 to 10 c.c. are mixed
with the solution and the latter filtered after standing from
fifteen to thirty minutes.
2. Lead acetate with subsequent addition of alum or
aluminum sulphate, the lead sulphate formed carrying
down the foreign matter.
3. Aluminum hydrate in the form of a thin paste, of
which several c.c. are shaken with the solution.
4. Tannic acid, to precipitate albuminous substances.
This must be examined beforehand with regard to its
optical activity.
5. Charred blood or bone-black, to remove colouring-
matter, $\frac{1}{2}$ to 1 gm., are added to the liquid.

In some cases this clearing is difficult, and the method
best adapted must be determined by previous experi-
ments. For solutions prepared from candies the pasty
aluminum hydrate is the best medium.When, as is often the case, invert sugar is present, the
result of the direct polarisation will be too low on accountof the left handed rotation of this sugar. In such a case,
Clerget's inversion method must be applied to find the
correct per cent of sucrose. This is conducted as fol-
lows:—26.048 grms. are dissolved in a sugar flask and the
solution made up to 100 c.c.; 50 c.c. of this solution are
transferred by means of a pipette to a 50 or 55 c.c. flask,
cleared, and polarised, the reading being corrected for the
extra 5 c.c. The liquid adhering to the pipette is washed
into the 100 c.c. flask containing the remaining 50 c.c.
(13.024 grms.), 5 c.c. of concentrated hydrochloric acid
(38 per cent, specific gravity 1.88 at 15° C.) added, and the
flask heated for fifteen minutes at 67° to 70° C. in a water
bath. The temperature should not exceed this limit.
The flask is then cooled rapidly and the solution made up
to 100 c.c. If the liquid is coloured, it is shaken with $\frac{1}{2}$
to 1 gm. of bone-black, and filtered through a double
filter. It is then polarised in a 200 m.m. tube, which is
provided with a thermometer. As the rotatory power of
invert sugar is much influenced by the temperature, this
factor must be regarded. The reading is best taken be-
tween 18 and 22° C., and the temperature accurately
determined. The reading must also be doubled on ac-
count of the dilution of the liquid.To calculate per cent of sucrose (R) the two readings
are added together, the sum (S) multiplied by 100 and
divided by $142.4 - \frac{1}{2}t$; where t is the temperature at
which the invert reading was taken. If the temperature
is exactly 20° C., the result can be made more accurate
by substituting 142.66 for 142.4, thus:—

$$R = \frac{100 S}{142.66 - \frac{1}{2}t} = \frac{100 S}{132.66} = 0.7538 S.$$

If very much invert sugar is present, both the direct and
indirect readings must be taken at the same temperature.

I.—Chocolate.

Weigh out in a German silver dish 13.024 grms. of the
rasped chocolate, moisten with alcohol (to aid the solu-
tion in water), add 30 c.c. of water, and heat for ten to
fifteen minutes on the water bath. Filter while warm
into a 100 to 110 c.c. flask, using a folded filter, any tur-
bidity of the filtrate not being of any consequence. The
residue on the filter is washed with hot water until the
filtrate amounts to about 100 c.c. Five c.c. of lead
acetate are then added, the liquid allowed to stand fifteen
minutes, and a few drops of alum solution and some
moist aluminum hydrate added. The liquid is then
made up to 110 c.c., shaken well, and filtered through a
folded filter. Slight moistening of the filter will aid fil-
tration, but the first 25 c.c. of filtrate should then be
rejected. The polarisation should be increased by one-
tenth and then doubled.

II.—Candies and Confectionery.

(a) *Dragees* (seeds or kernels coated with sugar and
flour).—26.048 grms. are covered in a beaker with 40 to
50 c.c. of water and allowed to stand, stirring now and
then, until the mass is completely saturated. If the
liquid shows an acid reaction, some precipitated calcium
carbonate or a few drops of ammonia are added. The
larger particles are now separated by filtering through
cloth, the filtrate being collected in a 100 to 110 c.c. flask.
The residue on the filter is washed with cold water until
about 100 c.c. of the filtrate have accumulated. Some
aluminum hydrate is then added to clear it, the solution
made up to 110 c.c. with water, and about half a gm. of
bone-black added in case the liquid is coloured. It is
then allowed to stand half an hour, with occasional
shaking. The solution is finally filtered through a dry
folded filter.A preliminary test for invert sugar is made with copper
sulphate and soda-lye, and the solution analysed accord-
ingly. Dragees almost always contain invert sugar.(b) *Raffinade Wafers* (cane sugar, with ethereal oils
and colouring matter).—26.048 grms. dissolved in water,
made up to 100 c.c. in flask, and, if necessary, de-

coloured with bone-black. A preliminary test for invert sugar must always be made and the analysis directed accordingly.

(c) *Santonin Wafers* (worm wafers, cane sugar, with santonin and some agglutinant, as egg albumen).—13·024 grms. dissolved in a 100 c.c. flask (the santonin being insoluble), 5 c.c. of lead acetate added, with a few drops of alum solution, the solution allowed to stand some time, with occasional shaking, made up to 100 c.c. and filtered.

(d) *Dessert Bonbons* (Fondant's, Praline's, chocolate bonbons, consisting of cane sugar or invert sugar, serving as a covering for marmalade, fruit, or chocolate).—13·024 grms. are treated with water and a few drops of ammonium hydrate until dissolved. If only a slight residue remains the whole can be immediately transferred to a 100 c.c. flask, otherwise it must first be filtered. One-half of the liquid is inverted, the other polarised directly after having been cleared by means of aluminum hydrate in a 50 to 55 c.c. flask.

(e) *Marzipan Masse* (cane sugar, with crushed almonds).—13·024 grms. material are triturated in a porcelain mortar with cold water, then mixed in a flask with 50 c.c. of water and about 30 c.c. of pasty aluminum hydrate, well shaken, and filtered into a 200 c.c. flask. The residue on the filter is washed with water until the filtrate amounts to 200 c.c. As this candy contains no invert sugar, the solution can be polarised directly in the 200 m.m. tube, the reading being multiplied by 4 to correct for the dilution.

(f) *Cakes and Sweetened Pastry*.—26·048 grms. of the powdered material are mixed in a flask with about 75 c.c. alcohol (85 to 90 per cent) and allowed to stand one half hour in a warm place. It is then filtered through a fine cloth filter and the residue washed several times with alcohol. The filtrate is collected in a porcelain dish and heated on the water-bath until the alcohol has all been driven off. One half gm. bone-black is then added and the solution filtered into a 100 c.c. flask. 50 c.c. are used for inversion, the remained polarised directly.

(g) *Sugar-Coated and Preserved Fruits* (marmalade, compots, jellies).—A considerable amount of invert sugar and pectinous bodies are always present. The aqueous solution of the latter has no rotatory power. If the material is solid in consistence, a crushed or finely-cut average sample must be prepared. 13·024 grms. are then mixed with 30 to 50 c.c. of water and a few drops of ammonium hydrate (to neutralise any free vegetable acids), and allowed to stand several hours. It is then passed through a cloth filter into a 100 or 200 c.c. flask, the residue washed several times with hot water, and about 10 c.c. of aluminum hydrate and one half gm. bone-black added to the filtrate. It is then shaken and made up to the mark. After filtering the filtrate is polarised according to Clerget's method.

Fruit jellies and marmalade are analysed in a similar manner.

If the sucrose articles enumerated under II., g, was calculated by the formula—

$$R = \frac{100 S}{142'4 - \frac{1}{2}t},$$

we would only obtain the percentage present at the time of analysis. The acids of the fruit have, however, converted a large amount of the cane sugar originally used into invert sugar. The original percentage of cane sugar, which is taken as a basis for taxation by the Custom-house, can be calculated from the reading of the inverted solution. If this reading is referred to 26·048 grms. material dissolved in 100 c.c. and polarised in a 200 m.m. tube, we have the following relations if the above figure is called B:—

A solution of 26·048 grms. of cane sugar in 100 c.c. has, after inversion, at the temperature t° the left handed

rotation $42'4 - \frac{1}{2}t$. The amount of cane sugar corresponding to the observed polarisation B can thus be calculated by the proportion—

$$42'4 - \frac{1}{2}t : 26'048 = B : \frac{26'048 \cdot B}{42'4 - \frac{1}{2}t},$$

and this is contained in 26·048 grms. of the material used. Therefore the original percentage r of cane sugar can be calculated from the second proportion.

$$26'048 : \frac{26'048 \cdot B}{42'4 - \frac{1}{2}t} = 100 : r$$

whence—

$$r = \frac{100 B}{42'4 - \frac{1}{2}t}$$

If 13·024 grms. substance were used and the solutions polarised at exactly $20^{\circ}C$., then the following formula is more accurate:—

$$r = \frac{100 B}{42'66 - 10} = 3'062 B.$$

III.—Liquors.

The percentage of sugar in liquors is generally expressed as grms. per litre.

Every liquor must be previously tested for invert sugar by diluting a little in a test-tube with water, adding five drops of copper sulphate solution and enough sodium hydrate to form a clear blue liquid. If no change occurs upon heating, cane sugar only is present; a yellow or red precipitate indicates the presence of other sugars.

Liquors which do not contain invert sugar may be polarised directly in the 200 m.m. tube, being previously decolourised with bone-black if necessary. If a high percentage of sugar is present, the polarisation must be made in the 100 m.m. tube.

The presence of alcohol has no influence on the reading. The ethereal oils which are present, although optically active, are present in such small quantities as to be without influence. The grms. per litre (R) are found, when A is the reading in a 200 m.m. tube, by : $R = 2'6048 A$.

When invert sugar is present the alcohol must be removed, as it materially changes the rotation of this sugar.

Fifty c.c. of liquor are measured into a porcelain dish and evaporated to about one-half the volume on a water-bath. If the liquid has an acid reaction, a few drops of ammonium hydrate must be added before heating it. The residue is washed into a 100 c.c. flask and made up to the mark with water. One-half is then polarised directly, the other after inversion. Both solutions may have to be decolourised with bone-black.

Supposing—

V = number of c.c. used for analysis,

A = direct reading,

B = reading of inverted solution (both read in 200 m.m. tube),

t = temperature of inverted solution when polarised,

then the grms. of cane sugar (R) in a litre may be calculated from the formula—

$$R = \frac{26'048 (A - B)}{(142'4 - \frac{1}{2}t) V},$$

where, when the direct reading was +, the inverted reading —, the difference $A - B$ becomes $A + B$.

If the temperature was exactly $20^{\circ}C$.,—

$$R = 196'7 \frac{A+B}{V}, \text{ or more accurately } = 196'35 \frac{A+B}{V},$$

In liquors, as under III., b, the addition of the fruit juices may have caused inversion of a part of the cane sugar originally added. The original percentage of cane

sugar is then calculated from the inverted reading just as for candied fruits. The grms. of cane sugar (r) per litre are found from—

$$r = \frac{26.048 B}{(42.4 - \frac{1}{2} t) \bar{V}},$$

or when $t = 20^\circ$,—

$$r = 804 \frac{B}{\bar{V}}, \text{ or more accurately } = \frac{26.048 B}{32.66 \bar{V}} = 797.55 \frac{B}{\bar{V}}.$$

PLAN C.—Directions for Determining the Bonifications Value of Invert Sugar Syrup.

While the syrup is being barrelled, a number of samples are taken so as to obtain a good average. This is well mixed and 250 grms. weighed out in a tared beaker. After dissolving in distilled water, the beaker is placed on the balance and enough water added to bring the weight of syrup and water up to 1000 grms. The syrup has then been diluted with three times its weight of water. The solution is again well mixed with a glass rod and poured into a high cylinder. A special spindle is used to determine the percentage of invert sugar. This spindle is used similarly to the Brix spindle for analysing syrups. It is graduated at $17\frac{1}{2}^\circ \text{C.}$, and the following table is used to correct for the temperature:—

Subtract from the reading.	Brix.	Add to the reading.	Brix.	Add to the reading.	Brix.
At 10°C.	0.35°	At 18°C.	0.03°	At 25°C.	0.50°
11° C.	0.29°	19° C.	0.09°	26° C.	0.57°
12° C.	0.25°	20° C.	0.17°	27° C.	0.64°
13° C.	0.22°	21° C.	0.24°	28° C.	0.71°
14° C.	0.18°	22° C.	0.31°	29° C.	0.79°
15° C.	0.14°	23° C.	0.38°	30° C.	0.87°
16° C.	0.10°	24° C.	0.44°		
17° C.	0.04°				

The reading is multiplied by 4 to obtain the per cent of invert sugar in the undiluted syrup. Hundredths are always read as an additional tenth.

Example.—The spindle read 18.1 per cent invert sugar at 20° . Hence 0.17° must be added to the reading and the sum multiplied by 4.

$$18.1 + 0.17 = 18.27 \times 4 = 73.08, \text{ or } 73.10.$$

The weight of the cane sugar used in the preparation of the syrup is then calculated by subtracting 1-20th, and multiplying the result by the weight of the invert sugar syrup.

NOTICES OF BOOKS.

Chemistry of the Organic Dye-Staffs. By R. NIETZKI, Ph.D., Professor at the University of Basle. Translated, with additions, by A. COLLIN, Ph.D., and W. RICHARDSON. London: Gurney and Jackson (successors to Mr. Van Voorst).

THE value of Professor Nietzki's work has been widely recognised in Germany, and the translators merit the gratitude of all persons connected with the tinctorial industries for having executed the present version.

The author begins with a useful introduction, in which he explains the nature of chromophors, chromogens, and auxochromes. The respective theories of dyeing, the chemical and the mechanical, are stated, but no final conclusion is reached. The statement that vegetable fibres, in contradistinction to animal fibres, "require the intervention of a special mordant," though generally true is too sweeping. Carthamine we all know is readily taken up by cotton.

For determining the commercial value of a colouring-

matter, the author pronounces trial dyeings the only trustworthy method. This conclusion, in as far as it is well founded, is to be regretted. The working dyer, from prejudice or from more questionable motives, sometimes declares dye-ware supplied by some particular firm or firms inferior in quality. Hence processes of a different nature are exceedingly valuable for checking his assertions.

Prof. Nietzki divides the organic colouring-matters into fourteen groups, or rather into fifteen groups and a residue which so far refuses to be classified.

The reader when considering the vast number of coal-tar colours, actual or practical, must not suppose that all or even the majority of these are in practical use. Some, as it will be found in the work before us, have remained mere laboratory curiosities, others have been used for a time and then discarded as too fugitive, too costly, too difficult of application, or very often merely as possessing no distinctive advantages over others already in use.

Berberine is a curious instance of a natural dye-ware having basic properties capable of being fixed on the fibre like the basic aniline dyes. It is found naturally in calumba and barberry roots and belongs to the quinoline group of dyes.

In Chapter XV. the author considers the dye-ware of unknown constitution, most of which are natural products. Many of these, the author admits, are indispensable in dyeing, since no synthetical products have been able to do their work.

Against the use of bixin—in the form of annatto—for colouring butter and cheese we have protested elsewhere, on account of the loathsome manner in which it is often prepared. Bixin, in the crude material, is accompanied by another dye-ware, orelline, the composition of which has not yet been determined.

Curcume, the colouring principle of turmeric, is still extensively used. Unlike the majority of dyes, it is fixed upon cotton without the intervention of a mordant, though not very firmly. Mordants, indeed, by no means improve the turmeric shades either in fastness or brilliance.

It is unfortunate that all the attempts made to reduce the yellow colouring-matter of safflower into carthamine have so far failed.

Cochineal and also lac-dye have found their most dangerous rival in the scarlet-red azo-compounds.

In the present work it is pointed out that the colouring principle of lac-dye, laccainic acid, $\text{C}_{16}\text{H}_{12}\text{O}_8$, is distinct from that of cochineal.

The name Tyrian purple, here rightly applied to the colouring-matter of certain mollusca (*Purpura lapillus*, *P. hamastoma*, and *Murex sp.*), was unfortunately at one time applied to murexide. The confusion is of the less importance as a sufficient supply of uric acid for the production of murexide on the large scale was not available.

The so-called "patent colours" of Croissant and Bretonnière figure here under their French name of Cachon de Laval. Their very unpleasant smell, here noticed, is much complained of by many dyers.

Throughout this work the author deals "only with the general principles involved in the manufacture of individual dye-ware, as details for their technical production are untrustworthy, owing to the continuous developments taking place in the industry in question." On this fact there might be founded a very serious argument against granting patents for chemical inventions. Too many chemical patentees use their specification not as an ultimatum by which they are prepared to stand or fall, but as a screen behind which they can indulge in additions, omissions, or modifications.

For technical details, the author refers to Hummel's work. We hope that the joint undertaking of Professor Nietzki, Dr. Collin, and Mr. Richardson will prove signally successful.

CORRESPONDENCE.

A CURIOUS POINT IN THE HISTORY OF
THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—There is a very curious omission in the volume of the *Journal of the Chemical Society* for the year 1868. The Anniversary Meeting held March 30, 1868, is reported in the volume. The report begins on page 1, the first mention being that Mr. Warren de la Rue, F.R.S., President, in the Chair, read his report (which follows); then there is the balance sheet on page 36, but there is no mention whatever of the election of "officers and council for the ensuing year."

The question has arisen, "Did the Society elect officers and council for the period between March 30, 1868, and 1869?" Nowhere in the volume for the year 1868 is there the list of officers and members of the council.

As any Fellow of the Society who possesses early volumes of the journal may ascertain for himself, the custom used to be to publish the list of officers and council immediately after the address of the President. Why was that custom departed from in the year 1868? At that time I was a Fellow of the Society, and indeed from March, 1867, to March, 1868, I served as a member of the council. Whether I was in office or not from March, 1868, to March, 1869, I do not know; and there is (as I have said) nothing in print in the volumes of the journal which throws any light on the subject. There is a curious interest attached to this strange irregularity.—I am, &c.,

J. ALFRED WANKLYN.

ESTIMATION OF CAOUTCHOUC.

To the Editor of the Chemical News.

SIR,—Referring to the analysis of rubber by Mr. H. J. Phillips, published in the *CHEMICAL NEWS* for August 5, I note that caoutchouc is given as 54.26 per cent. It most probably is as much as that, but a considerable quantity, if not almost all, of this caoutchouc is old rubber worked up again, and has a very different effect to pure rubber.—I am, &c.,

J. K. BURBRIDGE.

Tottenham, August 15, 1892.

WANTED,—CONSISTENCY.

To the Editor of the Chemical News.

SIR,—I am under the impression that oft-times I have noticed in your columns a sad remonstrance with the authors of text books,—which you have been compelled to pass in the second class, albeit they aspire to pass others in the first class,—called forth by the use of the suffix *ic*, where it was in your opinion unnecessary and even misleading to the crammees.

It would be interesting, therefore, to hear on what grounds such an undoubted authority as the President of the Chemical Section of the British Association for the Advancement of Science employs the said suffix so glibly, and in an address which is itself somewhat of an appeal for consistency. Doubtless he has prepared magnesium sulphate and sodium chloride. I for one am on the tip-toe of expectation.—I am, &c.,

OVS.

Determination of the Specific Gravity of Sparingly Fluid Substances.—J. W. Bruehl (*Ber. Deuts. Chem. Gesell.*).—The author has devised a pyknometer with a neck wider than usual and with a lateral tube, to which a water air-pump can be attached.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

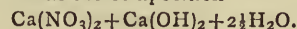
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 3, July 18, 1892.

Preparation and Properties of Carbon Diodide.—Henri Moissan.—To prepare this compound the pure tetraiodide of carbon is introduced into a very dry flask with a quantity of tetrachloride or of disulphide sufficient for its solution. It is refrigerated in a current of water, and the quantity of silver powder necessary to remove half the iodine is introduced in small portions. The flask is then sealed up, and the reaction is allowed to proceed in the cold until the liquid has merely a pale yellow colour. The protoiodide, C_2I_4 , forms fine crystals of a bright yellow colour, of specific gravity 4.38, fusible at 185° , and volatile without decomposition above their melting-point. It is very soluble in carbon disulphide; in the tetrachloride, and in ordinary ether, which, on cooling, deposits it in fine crystals. It is sparingly soluble in cold, anhydrous alcohol, but dissolves on boiling. It does not react with hydrogen; chlorine and iodine do not attack it in the cold, but in heat they form a bromiodide and a chloriodide. If heated in oxygen the protoiodide melts, and is then dissociated into iodine and carbon. At 110° it is not attacked by sulphur, but at higher temperatures iodine is eliminated and carbon disulphide is formed. It is not oxidised by boiling monohydrated nitric acid, by chromic acid, or by dilute solutions of permanganate.

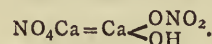
One of the Reactions of Spermine.—M. Duclaux.—The author shows that the alleged oxidising property of spermine is not special, but is common to all bodies which render water viscid or frothy, soap-lye, saponine, panamine, &c.

Election of a Foreign Associate of the Academy.—Herr Van Beneden was elected *vice* Sir George Airy by thirty-five votes, Professor Nordenskiöld receiving only three votes and Dr. Lister two.

A Basic Calcium Nitrate.—A. Werner.—The compound obtained has the composition—



On heating this substance to 160° in a U-tube in a current of dry air, it loses its water of crystallization and becomes—



Water immediately decomposes this salt. The existence of a basic salt formed by nitric acid combined with an alkaline substance like lime deserves attention as a mark of the kinship between the constitution of nitric acid and the phosphoric and arsenic acids.

The Efflorescence of Copper Sulphate and some other Metallic Sulphates.—H. Baubigny and E. Péchard.—The sulphates experimented on have been those of copper, cobalt, and zinc, beside the double sulphates of cobalt and potassium, zinc and potassium, ammonium alum, and chrome alum. According to the results of the authors in the simple sulphates studied, the rapidity of efflorescence may be considerably modified by the presence of small quantities of sulphuric acid in the liquid from which they have been crystallised. It will therefore be necessary when we wish to obtain stable hydrates for these sulphates to ascertain if their solution is perfectly neutral to methyl-orange.

The Decomposition of Basic Nitrates by Water.—G. Rousseau and G. Tite.—Last year the authors observed that copper subnitrate, if heated for some hours with water at from 150° to 160° , was entirely transformed into

copper oxide. They have since found that this decomposition has a certain generality. They have observed it in the basic nitrates of zinc, cadmium, and calcium, to which they now add bismuth and uranium.

The Phosphopalladic Compounds.—E. Fink.—M. Schützenberger has demonstrated the existence of a series of compounds containing platinum, phosphorus, and chlorine. The author has prepared similar compounds with palladium in place of platinum.

The Mechanical Contrast between the Radicle Cyanogen and the Halogenous Elements.—G. Hinrichs.—The author seeks to show that the monovalent radicle of cyanogen has not a composition of the same order as the simple and monovalent radicle of chlorine, or that it is impossible in mechanics to consider the elements as undecomposed radicles. In other words, the chemical elements, if they are complex substances, are not of the same order of composition as the common radicles.

Influence of the Methyl-Group, substituted for a Benzenic Hydrogen, upon the Properties of Orthotoluidine.—A. Rosenstiehl.—This paper will be inserted in full, if possible.

The Instability of Carboxyl in the Acid Phenols.—P. Cazeneuve.—The author finds that the instability of carboxyl united to a benzenic nucleus increases with the number of the phenolic hydroxyles which also occur in the molecule, and that the instability of the carboxyl seems to increase in the acid phenols with the substitutions—halogenous or other—in the nucleus. It is very probable that the general rule is that in the acid phenols the phenolic hydroxyles have a variable influence upon the stability of the carboxyl according to their position.

On Ferruginous Mineral Waters Preserved.—J. Riban.—The author maintains, very sensibly, that all discussion seems useless.

A New Leucomaine.—Dr. A. B. Griffiths.—The leucomaine in question, $C_{12}H_{16}N_2O_2$, is extracted from the urine of epileptic patients. It forms a crystalline hydrochlorate and chloraurate. With mercuric acid it gives a greenish white precipitate; with silver nitrate a yellowish precipitate, a white with phosphotungstic acid and a brownish white with phosphomolybdic acid, and a yellow with tannic acid. It is poisonous.

Journal für Praktische Chemie.
New Series, Vol. xlv., Parts 4, 5, and 6.

The Action of Alkalies upon the Iodalkylates of the Quinoline and Acridine Series.—Hermann Decker.—This bulky treatise does not admit of abstraction.

Nomenclature of Nitrogenous Nuclei.—O. Wiedman.—The author criticises the proposals of Knorr and of Hautsch.

Compounds of Chromammonium Sulphocyanide.—Odin T. Christensen.—A very full account of the reactions of Reinecke's salt (ammonium diamminchromsulphocyanide), $Cr_2NH_3(SCN)_3 \cdot NH_4SCN \cdot H_2O$.

Researches from the Laboratory of the University of Freiburg.—These consist of papers on γ -bromquinoline by Ad. Claus, and on the halogenalkylates of the oxyquinolines, and their decomposition by alkali and by silver oxide, by Ad. Claus and H. Howitz.

Contributions to the Chemistry of the Chromammonium Compounds; Chapter X. on the Rhodochrom Salts.—S. M. Jörgensen.

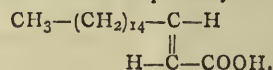
Constitution of the Cobalt, Chrome, and Rhodium Bases.—S. M. Jörgensen.—Both these memoirs, though very valuable, are unfit for abstraction.

A New Laboratory-Burner.—N. Teclu.—This paper requires the accompanying figure.

Analysis of the Julianen Brunnen and the Georgen Brunnen at the Eilsen Baths.—R. Fresenius.—Both these springs are very rich in sulphuretted hydrogen.

Experiments on the Preparation of New Organic Phosphorus Compounds.—Paul Heermann.—Although the author's researches do not definitely prove that phosphene or its derivatives, &c., are incapable of existence, they seem to show that the analogy of phosphorus and nitrogen here fails us and involves a decidedly different course of reaction, so that the compounds in question are produced either with difficulty or not at all.

Stereoisomerism of Oleic and Elaidic Acids.—Alex. Saytzeff.—Elaidic acid, like oleic acid, yields as its main product not oleic acid but an isomer, iso-oleic acid. Its stereochemical formula is probably—



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THE CHEMICAL NEWS.

VOL. LXVI., No. 1709.

NOTE ON THE LUMINOSITY OF HYDROCARBON FLAMES.*

By VIVIAN B. LEWES,
Royal Naval College, Greenwich.

EVER since Sir Humphry Davy, in 1817, advanced his celebrated theory as to the causes of luminosity of certain flames, the subject has commanded a great amount of attention, and the researches of Berzelius, Waldie, Volger, Hilgard, Landolt, Frankland, Stein, Heumann, Kersten, and more recently those of Soret, Birch, Stokes, and Smithells, have all added to our knowledge of the subject, but even now many points remain to be cleared up before we can gain a clear conception of the numerous factors and interactions which go to make up a luminous flame, and it is in hopes of raising a discussion upon some of these points that I venture to bring this paper before you.

Certainly the two most important land-marks in the history of luminous flames are the original enunciation of the solid particle theory by Davy and Frankland's celebrated attack upon that theory in 1868. The relative values of the views of these two great experimentalists have been so recently discussed that it would be useless to again go through the mass of evidence which has accumulated during the past twenty-five years, and which seems to point conclusively to the luminous flame of burning hydrocarbons, owing their power of emitting light to the presence of incandescent particles of practically pure carbon; whilst, on the other hand, I believe I am correct in saying that Dr. Frankland is unshaken in his belief that the cause of luminosity is to be found, not in solid particles of carbon, but in the incandescence of heavy hydrocarbon vapours.

In a paper read before the Chemical Society in January last, I described experiments and analyses which showed that the main reaction leading to luminosity in a flame containing hydrocarbons was the conversion in the inner non-luminous zone of the hydrocarbons into acetylene,—a change brought about by the baking action of the heat evolved by combustion in the outer layer of the flame, and in no way dependent upon oxidation, the change being entirely brought about by heat, as can be shown by passing the various gaseous hydrocarbons present in illuminating gases through heated tubes.

If an ordinary flat-flame be taken and the gases be carefully withdrawn from the non-luminous zone and analysed, the ratio of the acetylene formed, to the other unsaturated hydrocarbons, will be found to rapidly increase in their passage up the centre of the flame:—

Acetylene formed in the Inner Zone of a Flat-Flame from a No. 7 Bray Burner.

Portion of flame.	Total unsat. hydrocarbons.	Acetylene.	Other unsat. hydrocarbons.
	Per cent.	Per cent.	Per cent.
$\frac{1}{2}$ an inch from top of burner	3.565	0.115	3.450
$1\frac{1}{4}$ inches from burner ..	2.063	1.303	0.760
$1\frac{3}{4}$ " " " " ..	1.393	1.133	0.260
$2\frac{1}{2}$ " " " " ..	trace	trace	—

Showing that by the time the top of the non-luminous portion of the flame is reached over 81 per cent of the hydrocarbons present are converted into acetylene.

In such a flame luminosity commences just above the

inch and three-quarters above the burner, and if luminosity is caused by acetylene it is natural to ask why should it not have commenced at an inch and a quarter,—a spot where the acetylene is present in larger quantity than at the higher point. The reason for this is that in order to cause luminosity a temperature must be obtained at which the acetylene is dissociated, and the point at which this takes place marks the commencement of luminosity. If this temperature is not attained, then the acetylene in the presence of oxygen burns away with a non-luminous flame, or if no oxygen is present, polymerises into a number of higher hydrocarbons. If, on the other hand, a sufficiently high temperature is reached to cause dissociation, the liberated carbon becomes incandescent chiefly from its own combustion, but partly also from the combustion of the hydrogen liberated at the same time, and luminosity is the result.

The temperature needed to cause the dissociation of acetylene varies with the amount of dilution; the more diluted it is the higher being the temperature necessary to break it up, whilst the larger the quantity of acetylene the lower the temperature needed to cause its dissociation, and the smaller therefore the inner non-luminous zone of the flame.

In the flame from ordinary coal-gas there is only from 1.1—1.3 per cent of acetylene found in the inner zone, and in this highly diluted condition it requires a temperature of close upon 1200° C. to break it up, whilst in other flames richer in hydrocarbons, and therefore richer in acetylene in the inner zone, the temperature required is not so high; for example:—

Flame of—	Coal-gas.	Paraffin lamp.
Percentage of acetylene	1.133	2.222
Temperature at commencement of luminous zone	1267°	1062°

The fact that unless the requisite temperature is reached the acetylene burns away with non-luminous combustion is, I think, clearly shown by the following experiment.

The flame of burning alcohol contains more than half the quantity of acetylene that a good gas-flame contains, and yet the combustion is practically non-luminous. If a dish containing some alcohol be placed under a bell jar it burns with a flame having slightly luminous edges, and the temperature of the flame in this condition is 1220° C. If now a glass plate be put over the mouth of the bell jar for a few moments, the mixing of the products of combustion with the air lowers the rate of combustion, and the temperature of the flame falls to 1050° C., the flame becoming perfectly non-luminous, whilst if oxygen be admitted to the bell jar the combustion is increased and the temperature rapidly rises to 1510° C., the flame becoming nearly as luminous as a coal-gas flame, and depositing carbon on any cold surface held in it.

Again, if a small luminous gas-flame be allowed to play upon the bottom of a platinum dish, so much heat is abstracted from the flame that the temperature falls below the point necessary to break up the acetylene and the flame becomes non-luminous, whilst if the flame is allowed to remain in contact with the metal until the dish is red-hot the luminosity returns, and the same effect may be produced by heating the interior of the dish with a blowpipe flame. (This experiment was, I believe, devised by Heumann to show the effect of cooling on luminosity).

In every flame that I have examined which owes its luminosity to the presence of hydrocarbons, these bodies are converted into acetylene before luminosity commences in the flame, and every gaseous hydrocarbon which can by heat be made to deposit carbon is converted into acetylene before any deposition takes place.

Many of the hydrocarbons present in coal-gas are known to give out heat during their decomposition, but probably the most endothermic of these compounds is the acetylene, Thomsen having shown that no less than

* Read before the British Association, Edinburgh Meeting, 1892, Chemical Section.

55,010 units of heat are absorbed in the formation of 26 grains of acetylene, whilst only 10,880 disappear in the production of 28 grains of ethylene, and it is this which renders its decomposition by heat, or as shown by Berthelot, even by detonation into carbon and hydrogen, so easy.

The fact that acetylene is formed from the gaseous hydrocarbons present in illuminating gas prior to the emission of light does not, however, by itself in any way disprove Dr. Frankland's theory that luminosity is due to very heavy hydrocarbon vapours and not to solid particles of carbon, as the well-known tendency of the acetylene to polymerise into higher bodies might be taken as an explanation of the presence of sufficiently dense hydrocarbons in a flame given by, say, pure ethylene.

In order to determine whether or no the acetylene formed in the earlier stages of the flame renders the flame luminous by liberating carbon during dissociation as required by Davy's theory or by forming heavier hydrocarbons, a long series of experiments were made to ascertain the effect of heat upon the hydrocarbons present in coal-gas, and by specially devised apparatus to measure the actual temperature to which the gases were being heated, and to collect and analyse the resulting products. These experiments are still proceeding, but I may state the main results of them as being as follows:—

Ethylene passed at the rate of 4 to 5 c.c. per minute through a tube 2 inches in internal diameter undergoes no apparent change until the temperature rises to between 800° and 900° C.; it then breaks down to methane and acetylene; and simultaneously, with the formation of acetylene, heavy vapours appear which can be condensed, and in which benzene and naphthalene are conspicuous as well as a heavy and highly fluorescent oil of high boiling-point. Berthelot, found that these substances were formed when acetylene was heated for some time at the temperature at which glass softens, and he also recognised among the products cinnamene, C_8H_8 , and retene, $C_{18}H_{18}$, so that there seems very little doubt but that in passing the ethylene through a heated space in which the temperature does not rise above 900° C., methane and acetylene are first found and the latter at once polymerises into the heavier hydrocarbons. The amount of acetylene found in the products of the experiment of this temperature rarely exceeds 1 per cent, as the polymerisation occurs almost simultaneously with its formation, but the proportion of ethylene decomposed and the amount of methane found in the products of decomposition point to the initial action of heat at this temperature being: $3C_2H_4 = 2(C_2H_2) + 2(CH_4)$.

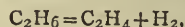
On increasing the temperature from 900° C. slowly up to 1000° C. the same action continues, no hydrogen appears in the products of decomposition, and no carbon is deposited, but the formation of oil and solid hydrocarbons is more abundant. Between 1000° and 11,000° C. a trace of hydrogen appears and a little carbon begins to deposit with the oil, this increasing with rise in temperature up to between 1300° and 1400° C., by which time all formation of oil has ceased. Carbon is deposited in larger quantities, and the residual gas consists of hydrogen with a little methane. The temperature at which oil disappears is about 1200° C., and the proportion of acetylene formed at this temperature is larger than at any of the lower ones.

It is evident, therefore, that if the temperature existing in the luminous portion of the flame exceeds 1200° C. the luminosity cannot be due to such hydrocarbons as are formed from the acetylene, but that carbon will be present in abundance.

I have made several analyses of the carbon so deposited and find that the hydrogen in it varies from 1 to 3 per cent, and as there is no fixed ratio, I think there is not the slightest foundation for imagining that it is in combination; indeed, Stein's work upon this point is fairly conclusive, and anyone who has attempted to prepare hydrogen free carbon from sugar, or other similar body,

will realise the intense power which freshly liberated carbon has of occluding and holding hydrogen.

Ethane, which is present in illuminating gas in larger proportion than is generally supposed, breaks up even below 800° C. into ethylene and hydrogen—



and the ethylene behaves as before on increase of temperature. Methane, which is only present in very large quantities in the original gas, but is also produced during the decomposition of the ethylene, is apparently unaffected by heat until a temperature of 1000° C. is reached when hydrogen and unsaturated hydrocarbons begin to appear in small traces. Acetylene being the chief of these, this action continues and increases, so that at about 1500° C. considerable quantities of acetylene are formed which at once break down to hydrogen and carbon. With methane, as with ethylene, the first trace of acetylene found in the products is also accompanied by the formation of oils and heavy condensable vapours. Methane is not so easily converted into acetylene as the other hydrocarbons, and requires a higher temperature to bring about the change; but the fact that it does so at high temperatures fully explains the facts first observed by Dr. Percy Frankland and Mr. Lewis Thompson, that although methane when burnt by itself has but a very feeble power of illumination, yet that when used as a diluent of heavier hydrocarbons it greatly increases the light emitting power of the flame.

In order to apply the knowledge these experiments give of the changes taking place in the hydrocarbons present in coal-gas during their flow through the heated channel in the interior of the flame, it is necessary to map out the temperatures existing in a luminous flame, and the flat-flame from a Bray burner (No. 7) lends itself conveniently to this purpose.

Using the Le Chatelier thermo-couple described by Dr. Roberts-Austen at the last meeting of the British Association, and making only one short twist of the wires to give contact, and then coating them with hard glass, it is possible for nearly a minute to get the temperature in the portion of the flame in which the short twist is plunged, and if thin wires are used the loss by conduction is very small. Of course, if the part of the flame through which the glass coated wires pass are at a higher temperature than the portion around the twist, as the heat penetrates the glass it will give too high a reading, but for the first thirty or forty seconds there is no fear of this.

With this arrangement I was able to map out the temperatures existing in the flat-flame, in which I had traced out the changes taking place in the constituents of the gas; and I found that the temperature rapidly rose from 500° C. half an inch above the burner to a little over 1200° C. at the commencement of the luminous zone—the luminous edges having a temperature of 1216° C.; and these temperatures were further increased in the luminous zone until near the top of the flame 1368° C. was reached. This at once gives us the secret of the luminosity. From the mouth of the jet and up to a temperature of 1000° to 1200° C., we have the formation of acetylene from the original hydrocarbons; but the moment the requisite temperature is reached by the combustion of the hydrogen and the carbon monoxide, the acetylene decomposes with a further rise of temperature, and the carbon, heated to incandescence, radiates heat and light.

In the experiments with the hydrocarbons the gases were passing through a heated space six inches long kept at a constant temperature; in the flame they are passing through a space 1.75 inches long with a rapidly increasing temperature, so that instead of the acetylene becoming polymerised to any great extent, it reaches a temperature at which dissociation takes place almost immediately it is formed.

Experiments with hydrogen-borne benzene vapour show

that at a temperature of 1200° to 1300° C. it is reconverted to acetylene, and this then at once breaks down to carbon and hydrogen, and the same happens with any other heavy vapours formed in the inner zone, and these bodies formed probably in minute quantities by polymerisation, together with any remaining methane, are reconverted into acetylene and deposit their carbon as soon as the necessary temperature is reached, and this supplies a fresh quantity of carbon particles to the upper portion of the luminous zone and so increases its size.

The careful analyses of Hilgard, Landolt, and Blochmann, made to determine the interactions taking place in various flames, are in their main features in close accord with a long series of analyses of the flame gases which I have made, and one of the most striking features of these is the comparatively slow rate at which the heavy hydrocarbons disappear, as compared with the other constituents of the original gas. This I find to be chiefly due to diffusion, which causes the hydrogen and methane to find their way to the outer skin of the flame first, and it is these bodies, therefore, which bear the brunt of the earlier combustion and yield the heat which bake the heavy hydrocarbons ascending straight upwards from the burner into acetylene.

If three concentric tubes be placed half an inch above an open tube from which coal-gas is issuing, and the gas from each is withdrawn and analysed, it will be found that on comparing them with the original gas the action is most marked. The gas in the outer tube being practically a mixture of air with hydrogen and methane and no heavy hydrocarbons, whilst in the inner tube the unsaturated hydrocarbons have risen from 3.56 to 4.53.

All analyses of the flame gases also show that the hydrogen burns first, and that next in rapidity of burning is the methane, and Prof. Smithells advances the theory that in the incomplete combustion taking place in the flame the hydrocarbons burn to carbon monoxide and hydrogen.

As has been already shown, the proportion of heavy hydrocarbons consumed before conversion into acetylene and then dissociation into carbon and hydrogen is very small, and the principal hydrocarbon undergoing combustion in the flame is methane. The analyses of Landolt, Hilgard, Blochmann, myself, and Smithells all show that a large increase in the carbon monoxide undoubtedly does take place; the higher one ascends in the flame until the luminous portion is reached, and also it is probable from the same analyses that hydrogen is generated by some action in the outer layer of combustion, as in spite of its rapid combustion at the base of the flame, as shown by the large percentage of water vapour formed there, it keeps reappearing for some little distance up the flame, and it is to explain the joint appearance of carbon monoxide and hydrogen that Prof. Smithells brings forward the theory that carbon burns to carbon monoxide, setting the hydrogen free from the hydrocarbons.

There is not the slightest doubt from the work done by Dalton, Blochmann, Kersten, E. von Meyer, and Dixon, that if you explode together gaseous hydrocarbons with a limited supply of oxygen you obtain carbon monoxide and hydrogen, and it is also probable from H. H. Baker's experiments that carbon burns first to carbon monoxide, but I fail to see that any such theory is necessary to explain the actions taking place in a flame. If we analyse the gases present in the flame $\frac{1}{4}$ of an inch above the burner, which is about the point at which increase of carbon monoxide commences, although it is not marked until $1\frac{1}{4}$ inches up the flame, we find that in the outer zone of the flame we have—

Water-vapour		24.65 per cent.
Methane		8.35 ..

A little deeper in the flame we get—

Water-vapour		17.94 per cent.
Methane		21.51 ..

and from this point up to $1\frac{1}{4}$ inches you have the temperature rapidly rising from 750° C. to 1100° C., and it is a well-known fact that if heavy hydrocarbons and water vapour are heated together they yield carbon monoxide and hydrogen; indeed, it is the most expensive method of making water-gas, and wrecked one process for the manufacture of illuminating water-gas, and one would expect the same thing to happen when methane and water-vapour are heated to this temperature.

In order to try if this were so, methane was passed through water just below the boiling-point and then through a tube heated to 1000° C., the resulting gases being then analysed, when it was found that the methane and water-vapour had interacted to form hydrogen, carbon monoxide, and carbon dioxide, and I should think that this is a far more likely cause of the effects produced in the flame.

Taking the facts which I have now laid before you, we may, I think, fairly fully explain the actions that take place in the flame and lead to luminosity. As the gas leaves the jet, the hydrogen rapidly diffuses to the outer edge of the flame and burns, the methane doing the same but rather more slowly. The combustion of these gases raises the temperature 500° C. in the first half inch, while before another half inch has been traversed 1000° C. is reached, and the chemical changes in the hydrocarbons are progressing rapidly, the unsaturated hydrocarbons and higher members of the saturated hydrocarbons being rapidly converted into acetylene. If the temperatures of the flame were not allowed to rise above 1000° C. this acetylene would be nearly all polymerised into benzene, naphthalene, diphenyl, and other complex bodies, which would be slowly burnt up without liberation of carbon, and a non-luminous flame would result. In the case of a gas flame, however, instead of remaining at 1000° C. the temperature rapidly rises to 1200° C., with the result that instead of polymerising into more complex bodies most of the acetylene formed at once splits up into carbon and hydrogen, and the former heated to incandescence by combustion gives the luminosity. It is the attainment of this temperature that marks the limit of the non-luminous zone. If this were the only action, however, the luminous zone would be very short. The bodies, however, formed from the acetylene before 1200° C. was reached, and the methane, of which some still remains unburnt, are converted into acetylene at a still higher temperature, *i.e.*, 1300° C., and this being reached near the top of the luminous zone yields a fresh supply of carbon, and so increases the height of the light-yielding portion of the flame.

In producing the luminous flame, therefore, there are two main factors to be observed: first, to use such compounds as shall be most easily converted into acetylene, and secondly, to attain as quickly as possible as high a temperature as practicable.

A NEW METHOD FOR MEASURING THE PRESSURE PRODUCED IN GASEOUS EXPLOSIONS.*

By BEVAN LEAN, B.A., B.Sc.,
Dalton Chemical Scholar of the Owens College,
and W. A. BONE, B.Sc., Fellow of Victoria University.

THE authors have devised a new method by which they hope to be able to measure the pressure produced on the explosion of gaseous mixtures. All former measurements involve the motion of a guage of considerable mass. Bunsen measured the pressure developed by studying the limiting weight raised by a valve attached to a bomb. Berthelot and Vieille determined the rate of displacement

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

of a piston of known section and mass. Mallard and Le Chatelier have employed a Deprez manometer, and also a metallic Bourdon gauge. Dugald Clerk has made use of a Richards indicator. In consequence of the instantaneous character of gaseous explosions it is doubtful whether, by the means employed by these experimenters, it is possible to measure the *real* pressure produced by the explosion. Their methods would appear to measure no more than the effective pressure.

The authors announce preliminary experiments in which they have studied the pressure produced by a mixture of two volumes of hydrogen with one volume of oxygen.

They attached to a leaden coil of two litres capacity a strong glass tube of from 10 to 25 c.c. capacity, closed at one end, and separated at its other end from the coil by a gas-tight steel cap, the bore of which had the same diameter as the glass tube. The glass gauge had previously been calibrated and graduated. The coil was then filled with the explosive mixture, while the glass gauge was filled with air or hydrogen. The instant the mixture was fired the tap separating the coil from the gauge was opened, and the flash due to the exploding gases darted into the gauge. The experiment consisted in taking a photograph upon a sensitive plate of the flash in the gauge. It was found possible to obtain photographs which showed the flash to come to a well-defined and abrupt termination, marking the volume into which the air in the gauge had been compressed. By this means the authors hold that the air in the gauge is compressed adiabatically, and with the data afforded by the photograph they contend that it is possible to calculate the pressure produced in the explosion by Rankine's well-known formula—

$$P' = P \left(\frac{V}{V'} \right)^{\kappa}.$$

The assumption is therefore made that there is no loss of heat up to the time that the flash attains its furthest limit. To obtain some data to justify this assumption, the authors took a photograph of the flash upon a swinging plate attached to a pendulum chronograph. The plate moved past the flash at the rate of $2\frac{1}{2}$ metres per second. The photographs so obtained could scarcely be distinguished from those taken upon a stationary plate; they were perfectly symmetrical, only the slightest possible increase in breadth could be detected. These photographs showed that the compression is approximately instantaneous, and that the flash ceases to have any sensible photo-chemical action in an interval of time less than one five-thousandth of a second. In so short an interval of time the compressed gas cannot lose a sensible quantity of heat. It would appear, therefore, right to assume that the compression is adiabatic. The authors believe also that no appreciable diffusion of the compressed gas into the compressing gas can occur during the very brief time of compression.

Further, since thermo-dynamic theory proves the ratio of the two specific heats of any perfect gas to be approximately constant for all temperatures and pressures, Rankine's formula may be employed to calculate the pressure produced by the explosion when the gauge is filled with air or hydrogen.

Essentially, therefore, the method gives a record of the adiabatic compression of a gas by the explosion, a piston of indefinitely small thickness and mass being interposed between the compressed and compressing gases.

Experiments have been made with gauges of different volume, varying from 11.55 c.c. to 23.20 c.c., and the ratio $\frac{V}{V'}$ is found to be independent within these limits of

the volume of the gauge. Further, the ratio $\frac{V'}{V}$ is found to be the same, within the error of experiment, whether air or hydrogen is the gas compressed. The photographs obtained, however, in the case of hydrogen, show the flash to be in general ill-defined and pointed, owing

probably to the high thermal conductivity of hydrogen, combined with a much greater inter-diffusion with the compressing gases in consequence of the greater molecular velocity of hydrogen in comparison with that of hot air.

The mean value from six different sets of experiments with air and hydrogen, electrolytic gas being the explosive mixture, gave $\frac{V}{V'} = 8.6$. Calculating P' by means of

Rankine's formula, and taking $\kappa = 1.408$, it is found that $P' = 20.7$ atmospheres. This pressure is about twice that measured by former experimenters. Some experiments were also made with carbonic acid gas; in these the explosion compressed the gas into a much smaller volume, owing to the great variation of the two specific heats of carbonic acid gas with increase of temperature and pressure.

The authors desire to state that the idea upon which their method is based was suggested to them by Professor H. B. Dixon.

WATER ANALYSIS.

By J. ALFRED WANKLYN.

FROM a letter of Dr. Frankland's which has been recently published it would appear that that eminent chemist (who succeeded the late Mr. Way as chemist on the Royal Commission on the Pollution of Rivers, and the late Professor Hofmann, as chemical contributor to the Registrar General's Annual Report) has quite recently been made Chemical Adviser to the Local Government Board. It would seem, moreover, that in this last official capacity he has been employed in endeavouring to disparage and discredit the ammonia process and in forcing his own process upon reluctant analysts. Under these circumstances I have to take up the controversy which was carried on at the meetings of the Chemical Society in the years 1868 and 1876; and to urge afresh the reasons against Dr. Frankland's process and in favour of our process.

Dr. Frankland's process consists in taking a given quantity of water, evaporating it down to dryness (the nitrates being reduced during the evaporation by sulphurous acid), and finally performing elementary organic analysis on the water residue. From the carbonic acid so obtained the carbon is calculated and called "*organic carbon*," and the nitrogen gas so obtained is measured and called "*organic nitrogen*"; and these two data are, if Dr. Frankland is allowed to have his way, to become the criteria of the purity or otherwise of drinking water. I believe it would be most disastrous and injurious to the good name of English chemists if such an event should take place, and will now recall to mind the objections to the Frankland water analysis.

The first objection is that the process, as he works it, is invalid. It will be obvious to most people that a process which burns up a water residue and confines itself to measuring the carbonic acid and nitrogen so generated cannot measure the carbon and nitrogen in any organic matter which volatilises during the evaporation of the water. Equally obvious to most people will it be that in so far as the non-volatile organic matter undergoes decomposition during the evaporation, in so far it will be liable to escape registration when the water residue is submitted to the final combustion. Frankland's process is in fact confined to such organic matter as survives the evaporation, and at its best could only give the organic carbon and organic nitrogen in water residues—which is a very different thing from the organic carbon and nitrogen in the original water.

Now, having obtained a dry water residue, free from carbonates and nitrates, there would be no difficulty in ascertaining the actual weight of carbon or nitrogen by applying to it the ordinary elementary organic analysis, which is one of the best known, and most accurate and

trustworthy of all processes. But elementary organic analysis is only valid when certain essential conditions are complied with. Chief among such conditions is that the combustion should be carried out on a proper scale—that the burning of too little organic matter should be avoided. Frankland burns up the residue from one litre (and I believe in some instances from less than one litre of water), but the organic matter in the water residue from one litre of drinking water is too little to give a real result, and the failure to operate upon a sufficiently large water residue renders his water analysis invalid, even as a process for the ascertainment of the organic carbon and nitrogen in a water residue.

Now it may be asked why should not Frankland evaporate down ten litres instead of only one litre, and so obtain a residue which would contain enough organic matter? In a week or a fortnight at the outside the evaporation of ten litres might be accomplished without being obliged to increase the size of the evaporating dish. To Dr. Frankland time and trouble and cost are of no account.

The real reason against any increase of the scale of the operation is that it would bring Dr. Frankland face to face with an irresistible proof of the fundamental and inherent vanity of his water analysis. Nothing is more likely than that the water residue from ten litres of common drinking water would contain as much organic carbon and nitrogen as could be got from the residue of twenty litres of the same kind of drinking water. I fancy that Dr. Frankland feels that something of that kind would happen, and that his faith in his own process would vanish along with the organic matter, which would suffer destruction on prolonged evaporation of many litres of drinking water.

Instead of burning the water residue left by many litres of water, and in that manner complying with the condition essential to the genuineness of the results, Dr. Frankland has sought so to modify the process of elementary organic analysis as to diminish the quantity of organic matter required for combustion. Fortunately, he published ten examples wherein small quantities of sugar, urea, and hippuric acid were burnt, and, as I pointed out at the meeting of the Chemical Society in the year 1863, the fact came out plainly enough that his modification of elementary organic analysis had not effected any real diminution of the error of experiment. His apparatus for the measurement of nitrogen and carbon would indicate 0.001 m.grm. of nitrogen and 0.0005 m.grm. of carbon; but the actual practical error of experiment as exhibited in his test analyses amounts to tenths of a m.grm., and even to a whole m.grm.; and in calling attention to it at the time, I could not help remarking that the actual performance appeared to be a satire upon his beautiful instrument.

In the practical working of his process, each analyst is directed to perform several blank operations "so as to be able accurately to correct for the combined errors of his own manipulation and apparatus." In Frankland's laboratory the correction actually came up to 0.32 m.grm. of carbon and 0.045 m.grm. of nitrogen per litre of water. A personal error of that magnitude is a satire on measurements claiming to be accurate to the thousandth of a m.grm. Persistent working where the personal error is so large and the measurements so delicate, and where, moreover, the operations are so tedious and laborious that they have to be almost wholly entrusted to assistants, leads to strange results, and in due course landed the Royal Commission on the Pollution of Rivers at the celebrated experiments on sulphate of quinine, which formed the subject of a correspondence in the CHEMICAL NEWS. In those experiments certain quantities of sulphate of quinine were dissolved in water, and the solutions of quinine were evaporated to dryness and the residues burnt, and the organic carbon and nitrogen arrived at. The experimental carbon and nitrogen agreed exactly with the calculated quantities, but the calculated quantities were wrongly calculated. And in that manner

the real nature of the results flowing from the Frankland water-analysis was exhibited in a most striking manner. Nothing, however, is more conclusive than the results of the examination of the water of Bala Lake. This water was at one time thought of as a possible supply for London, and punctually the Frankland method exhibited organic nitrogen 0.01 m.grm. per litre. Bala Lake water is not by any means pure water. It yields 0.25 m.grm. of albumenoid ammonia per litre, and the real quantity of nitrogen existing in organic combination in a litre cannot have fallen short of 0.20 m.grm.

New Malden, Surrey,
Aug. 16, 1892.

ANALYSIS OF COPAL RESINS.

By ED. KRESSEL.

(Continued from p. 91).

THE melting-point of copal resins varies from 175° to 370° C. When carefully roasted, at first a small quantity of gas, about 4 to 5 per cent, is obtained, which consists of—

	I.	II.
CH ₄	40.30	41.27
CO ₂	23.57	23.85
CO	36.13	34.88
	100.00	100.00

Heating further the copal oil distils over. I have made many careful experiments in order to estimate what loss in weight must occur before a soluble resin, fit for further manufacture of varnishes, can be obtained, and I have found it to be on an average from 8 to 12.5 per cent, but when the roasting process is carefully conducted, the loss need not exceed 10 per cent, and the raw product is fully converted into the soluble "pyro-copal."

Naturally when a closed vessel is in use for roasting the vapours are condensed, the copal oil thus collected and used otherwise. It must not be understood that the solubility of a copal resin depends upon the absence of the copal oil or a certain portion thereof, for we have seen before, on extracting the copal oil with ether from the raw copal, the swell copal was left as an insoluble matter, and still required the necessary high temperature to be converted into the soluble pyro-resin.

When the melting-point is reached the heat should so be regulated that the temperature does not increase by any way and be only slowly kept up; the mass will soon flow evenly, and after about 15 to 20 minutes the whole is sufficiently treated to be ready for further manufacture. Certainly the time is calculated for about 10 to 12 pounds of raw copal, and more time would be required should larger quantities be treated at once.

Quite analogous with this process is the conversion of starch into soluble dextrin; the former is heated to about 150°, and if a small quantity of HNO₃ or HCl is added to the starch the transformation takes place much more rapidly. This is also the case with copal, though on this point I will speak later on, as my investigations are not completed in that way at present.

The analysis of the carefully roasted (at 352° C.) soluble product, "pyro-copal," gave:—

	I.	II.	Average.
C	83.29	83.05	83.17
H	10.55	10.73	10.64
O	6.16	6.22	6.19
	100.00	100.00	100.00

The heat increased to 365° C.—

	I.	II.	Average.
C	84.23	84.37	84.30
H	10.76	10.73	10.745
O	5.01	4.90	4.955
	100.00	100.00	100.00

The heat increased to 375° C.—

	I.	II.	Average.
C.. ..	85'05	85'07	85'06
H.. ..	10'85	10'85	10'85
O.. ..	4'10	4'08	4'09
	100'00	100'00	100'00

From the chloroform solution of pyro-copal alcohol precipitates the pyro-swell copal. The substance dried at 100° C. gave—

	I.	II.	Average.
C.. ..	82'87	82'85	82'86
H.. ..	10'63	10'78	10'705
O.. ..	7'50	7'37	7'435
	100'00	100'00	100'00

Comparing now the raw copal with the pyro-copal and the swell copal with the pyro-swell copal, we find that roasting causes in every instance an increase of C. and a decrease of O, while the H remains nearly constant.

ON THE

DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

WITHIN recent years theories have been advanced by Kohlrausch, Ostwald, and others, as to the state in which salts exist in solution, which at first sight appear to be startlingly contradictory to all previous ideas on the subject, and which might well be considered to revolutionise chemistry. So numerous and so powerful are the proofs in favour of these theories, however, that in spite of many seeming objections one can scarcely doubt their validity. Each new series of experiments made on the subject seems to afford an additional proof; it is hoped that the results of the experiments detailed in this paper may be considered as still another.

If a dilute solution of a coloured salt—as copper sulphate, for instance—contains less molecules of copper sulphate as such than a more concentrated solution, owing to dissociation of the salt into its ions Cu and SO₄, it follows, if no other influences are at work, that with equal quantities of salt present in each solution, the colour of the dilute solution must be lighter than that of the more concentrated solution, and that, too, in proportion to the amounts of copper sulphate molecules dissociated into their ions. It is possible that the ions themselves of coloured salts may form coloured solutions, and so the colour of a dissociated salt may not be any different from that of the undissociated salt. The probability of this being the case will be discussed further on. If, however, experiment actually shows that dilute solutions of coloured salts are more than proportionately light in colour than concentrated solutions, there is a great probability that it is due to dissociation in solution. To test this, solutions of some thirty-five coloured salts were compared with each other colorimetrically at different dilutions. The influence of temperature on the colour effects of the different solutions was also determined.

The colorimeter used consisted of two graduated glass tubes with flat bottoms about 2.5 c.m. in diameter. One tube had a tubulure near the bottom, connected by india-rubber tubing to a vessel capable of being moved up and down vertically in a clamp, so that the volume of liquid in the tube could be altered at will. Each of the tubes was carefully calibrated, and the corrections to be applied for each volume in both the vessels determined. The required volume of the more concentrated of the two solutions to be compared was run from the burette into the non-tubulated vessel, and the volume of liquid in the

tubulated vessel varied till of the same tint. The two tubes stood on a plate of clear glass, and light was reflected up the tubes from underneath by a sheet of white paper stretched on a plate arranged at the angle reflecting the greatest quantity of light. A sheet of paper is much to be preferred to a plate of white porcelain or to a mirror, as these reflect images of any objects coming across their path, and so do not give a uniformly illuminated surface.

All colour comparisons were made at a window through which no direct sunlight entered. The solutions in the two tubes were viewed vertically from above through a piece of white cardboard with two circular holes cut in it, so that two uniformly illuminated surfaces of the solutions were seen. It was found that with practice colours could be judged correctly in almost all cases to within three per cent, and, as in comparing solutions at different dilutions, four or more separate observations with different volumes of solution were made, the values are in most cases accurate to within two per cent or less. After getting the solutions as nearly of the same tint as possible, it was found best to turn the eye to some different object altogether, especially one of a colour complementary to that of the solution under examination, and then after a few seconds to again examine the solutions, when it was frequently found that they were not accurately compared the first time. The same process was repeated twice more before the comparison was finally considered as correct. With deeply coloured solutions, the mask through which the solutions were viewed was protected from the light by a shade, when, from contrast with the now darkened mask, the comparison was rendered much more easy. With very dilute solutions, the intensity of the light reflected up the tubes was decreased by interposing a piece of tracing paper in the path of the light from the window. The salts used were not specially purified, but the purest specimens obtainable from the manufacturers were always used.

The Change of Colour Effect on Dilution.

The method of procedure was as follows:—100 c.c. of the normal solution was made up, and 25 c.c. of this was diluted to 125 c.c., whereby a solution of 5 litres dilution was obtained; 7 c.c. of the normal solution was introduced from a burette into the non-tubulated vessel, and the colour comparison with the 5 litres solution made; 3 c.c. more of the normal solution was then introduced, and another comparison made, and so on. A decinormal solution was then made up and compared with the normal solution. Centinormal solutions were compared with the decinormal, and millinormal with the centinormal.

The salts examined consisted of the sulphates, chlorides, and nitrates of the metals copper, nickel, cobalt, chromium, and uranium, together with the acetates of three metals, and also several organic salts of iron. These salts were chosen in order to determine whether any general relations existed between the changes of colour effect on dilution and the nature of the acids and bases composing the salts.

Five copper salts were examined. From the table it will be seen that the solutions of all the salts decrease in colour effect on dilution, the sulphate the least, then the chloride, chlorate, nitrate, and lastly the acetate, which decreases very greatly on dilution. The reason of this will be indicated further on. None of the salts of either copper, nickel, cobalt, or uranium showed deep enough tints to make determinations at dilutions of 1000 litres possible. Nickel salts show much less colour decrease than copper salts, neither the sulphate nor the chloride showing more than a barely appreciable decrease at a dilution of 10 litres. All the cobalt salts dissociate considerably more than the corresponding salts of both nickel and copper; but in this case, though the sulphate is the least dissociable, it is the chloride and not the nitrate that is the most dissociable. The same thing holds for uranyl salts, the sulphate being less dissociable than the nitrate, and this again than the chloride. These

Substance.	Colourations at dilutions.							Dilution in litres.	Chromium sulphate.	Chrome alum.	Chromium chloride.	Cobalt sulphate.	Iodine.
	1.	25.	5.	10.	50.	100.	1000.						
Cupric sulphate ..	100	—	98.3	95.1	—	93.0	—	10	100	100	100	100	100
„ chloride ..	100	—	98.4	91.0	—	88.2	—	20	100.7	96.6	100.9	97.5	95.0
„ nitrate ..	100	—	87.4	85.9	—	81.2	—	30	101.3	92.7	100.0	92.0	94.7
„ chlorate ..	100	—	90.7	89.6	—	84.9	—	40	98.9	92.2	99.1	90.5	93.5
„ acetate ..	—	100	82.7	68.2	—	37.1	—	50	98.2	93.8	98.0	90.0	90.7
Nickel sulphate ..	100	—	100.1	98.5	86.2	—	—	70	99.4	92.7	100.6	89.6	90.7
„ chloride ..	100	—	99.1	97.5	94.5	—	—	100	97.4	90.0	99.8	89.2	92.4
„ nitrate ..	100	—	97.3	94.1	83.2	—	—	120	96.0	87.4	100.1	87.8	93.8
Cobalt sulphate ..	100	—	90.8	89.2	—	77.8	—	150	95.8	87.5	101.1	86.5	94.0
„ chloride ..	100	—	87.9	76.4	—	65.5	—	180	96.1	85.6	100.4	85.7	94.5
„ nitrate ..	100	—	93.1	89.4	—	79.2	—	200	95.5	87.2	101.2	84.6	94.0
Uranyl sulphate ..	—	100	97.1	91.9	—	86.7	—	300	96.2	90.3	100.2	83.7	94.5
„ chloride ..	—	100	90.0	82.6	—	78.4	—	400	98.1	92.6	101.5	82.8	95.0
„ nitrate ..	—	100	98.1	90.9	—	85.6	—	500	99.0	90.8	103.0	82.0	95.3
„ acetate ..	—	100	98.5	96.9	—	92.1	—	600	103.0	92.0	104.3	80.7	96.1
Chrome alum ..	—	—	—	100	84.5	91.6	90.6	700	104.7	90.0	108.2	79.0	98.3
Chromic sulphate ..	—	—	—	100	94.4	99.8	91.1	800	110.2	90.6	—	78.5	98.2
„ chloride ..	—	—	—	100	98.6	94.7	90.6	1000	110.2	—	—	77.8	99.9
„ nitrate ..	—	—	—	100	121.8	107.2	—						
Iodine ..	—	—	—	100	—	95.2	115.2						
Potassium chromate	100	—	101.9	102.9	—	100.8	103.6						
Potassium bichromate ..	—	—	100	97.4	—	85.0	73.9						
Chromium trioxide ..	100	—	79.4	69.1	—	59.3	42.9						
Ferric chloride ..	100	—	160.5	208.3	—	246.8	—						
Ferric chloride + hydrochloric acid ..	—	—	100	70.5	—	16.3	5.4						
Ferric acetate ..	—	—	—	100	—	149.1	—						
„ citrate ..	—	—	100	101.3	—	133.2	—						
Ferric citrate + citric acid ..	—	—	—	100	—	131.1	176.7						
Ferric ammonium citrate ..	—	—	—	100	—	102.1	102.8						
Ferric oxalate ..	—	—	100	77.9	—	63.6	53.8						
„ tartrate ..	—	—	100	118.1	—	270.6	342.6						
Ferrous citrate ..	—	—	—	—	—	100	61.1						
Potassium ferrocyanide ..	—	100	98.8	97.2	—	—	—						
Potassium ferricyanide ..	—	—	—	—	—	—	—						
Potassium permanganate ..	100	—	98.1	93.5	—	89.1	88.5						

salts dissociate to a greater extent than copper salts, but not so much as cobalt salts. The acetate of uranium solution, however, shows a very different behaviour from that of acetate of copper, for it is the least dissociable of any of the uranyl salts examined. Chromium salts gave very extraordinary results, for the colour effect of their diluted solutions was found to depend on the method of dilution, according as it was sudden or gradual. Such results were afforded by no other solutions of salts examined. In the table are given the values obtained by diluting the solutions suddenly by adding all the water to the more concentrated solution at once. It will be seen that with solutions of chromium sulphate and chloride, and chrome alum, the colours at 50 litres dilution are considerably less than those at a dilution of 10 litres, but that on further dilution to 100 litres the colour increases, whilst it again decreases on still further dilution. Concentrated solutions of these three salts were then diluted gradually from 10 to 1000 litres, a colorimetric determination being made at each dilution. The results obtained were as follow in the table. The numbers in the last two columns will be referred to later on.

It will be seen that chromium sulphate solution decreases slightly in colour effect till a dilution of 200 litres, but that from this point it begins to increase again, till at 1000 litres it is considerably greater than the decinormal solution.

It is noticeable that the colour effects obtained by gradual dilution are quite different both in intensity and even in direction from those obtained by sudden dilution,

for with 1000 litres solutions in one case the colour effect is greater, and in the other less than the colourations of the 10 litres solutions. There is, however, a general resemblance between the colour effects of chromic sulphate and chrome alum solutions in the sudden dilution series, and also in the gradual dilution series. Chromium nitrate solution increases greatly in colour effect on sudden dilution from 50 to 100 litres, and decreases again on further dilution. These experiments with chromium salts were repeated, the same values being obtained, so they cannot be due to experimental error. Such extraordinary behaviour can only be explained on the supposition that hydrates of different composition and different colour effect are formed, according to the manner of dilution.

The only exception besides the chromium salts was found in the case of a solution of iodine dissolved in potassium iodide. The iodine was dissolved in a solution containing three times its weight of this salt. On dilution of the solution to 100 litres, the colour effect decreased, but after this point it began to increase, till at 300 litres dilution it had reached the value 107.3, and at 1000 litres that of 115.4. The solution was then examined by gradual dilution, when it was found that in the same manner the colour decreased up to a dilution of about 80 litres, and from this point began to increase again, but only slightly.

Both series of experiments were repeated and found to give the same results, so the variations cannot be due to experimental error. What they can be due to it is difficult to conceive. It may be that the decinormal solution contains a few molecules of I_4 , which up to a dilution of 100 litres are dissociated into I_2 molecules, but that on still further dilution these I_2 molecules begin to be dissociated into I molecules, with increase of colour effect. There are evidently two distinct reactions taking place in the solution; also it may be that the presence of potassium iodide in the solution has some influence, some peroxide being formed.

Several other salts were examined colorimetrically by gradual as well as by sudden dilution, but the same values were obtained in each case. The values found for cobalt sulphate are given as an example. The solutions are ten times more concentrated than the dilutions given.

(To be continued).

A New Stopper for Reagent Bottles.—A. Gawałowski.—The stopper has a mushroom shaped stopper to prevent dust from falling (nothing novel!), and is drawn out below to a point. A lateral cavity is ground in the lower part of the stopper to permit of the reagent being poured out in drops. The contact surfaces of the bottle and the neck are ground to prevent the stopper from sticking fast.—*Zeitsch. für Anal. Chemie*, xxx., Part vi.

ON THE
ESTIMATION OF URIC ACID IN URINE:
A NEW PROCESS BY MEANS OF
SATURATION WITH AMMONIUM
CHLORIDE.*

By F. GOWLAND HOPKINS, B.Sc.,
Gull Research Student at Guy's Hospital.

THE process to be described depends upon the following facts:—

1. Ammonium urate is wholly insoluble in saturated solutions of ammonium chloride.

2. If solutions, such as urine, which contain the mixed urates of different bases be saturated with ammonium chloride, the large mass-influence of the latter ensures the rapid and complete conversion of all the uric acid into biurate of ammonium, which, in accordance with (1), is, *pari passu*, thrown out of solution. In the case of urine, saturation with ammonium chloride is followed by a complete precipitation of the uric acid present in the course of two hours at most.

It has long been known that ammonia and salts of ammonia will, after long standing, so completely precipitate the uric acid from urine, that subsequent treatment with acids produces no further precipitate (Wetzlar, "Beiträge zur Kenntniss des menschlichen Harns," Frankfurt a.M. 1821, p. 19). Fokker, moreover, observed that when a solution of any urate is made alkaline, and then mixed with a solution of ammonium chloride, the uric acid slowly separates out as the biurate of ammonia. Upon this observation the well-known Fokker-Salkowski process is based.

But the crucial fact that saturation with the ammonium chloride renders the separation rapid and absolutely complete does not seem to have been previously observed. The importance of this fact in any attempt to estimate uric acid by means of its separation as ammonium urate will be seen when it is remembered that, hitherto, in all such processes, a large correction has to be made to allow for incomplete separation, even after long standing. In the Fokker-Salkowski process, for instance, the factor which has to be added to the result amounts to at least 25 per cent of the total variably dealt with,—a necessity which would seem to render the process of little scientific value (*vide* Fokker, *Pflüger's Archiv*, vol. x., p. 157, 1875; Salkowski, *Virchow's Archiv*, vol. lxxviii., p. 401, 1876). In the method about to be described no such correction is necessary.

The following experiments with pure urates will show the complete separation of ammonium urate which occurs after saturation with the chloride.

In each case pure uric acid, prepared by means of the sulphate, was used. The ammonium salt precipitated was decomposed by means of HCl, and the uric acid subsequently washed and weighed, due allowance being made for washings:—

	Uric acid recovered.
(1.) One decigram. of uric acid dissolved in ammonia, solution made up to 250 c.c., saturated with ammonium chloride, and filtered after 30 minutes.	0.0994
(2.) Fifty m.grms. dissolved as above and made up to 150 c.c. Filtered after 15 minutes.	0.0502
(3.) One decigram. dissolved in Na_2CO_3 , solution made up to 100 c.c. Filtered after 3 hours	0.0986
(4.) One decigram. dissolved as in (3). Filtered after 4 hours	0.0990

The presence of excess of bases, other than ammonia, delays the precipitation, but, as stated above, two hours

is amply sufficient in the case of urine. (*Vide* note (b), *infra*).

The process of estimation in urine may be carried out as follows:—

To 100 c.c. of the urine, finely-powdered pure ammonium chloride is added in excess, about 30 grms. being necessary. The solution is allowed to stand for two hours, with occasional stirring, and the precipitate then filtered off through a thin filter paper.

The precipitate is then washed with a saturated solution of ammonium chloride. If a few crystals of the solid salt used for precipitation are still undissolved at the time of filtration, it is of no disadvantage; the light flocculent urate is easily washed first on to the filter, the crystals being then dissolved in a minimum of distilled water and used for washings.

After it has been washed twice or thrice with the saturated chloride solution, the urate is washed off the paper into a small beaker by means of a jet of hot distilled water.

The ammonium urate is then decomposed by boiling with a slight excess of HCl, the solution concentrated, if necessary, and the uric acid allowed to separate out. It may be finally determined by any accustomed method (*Vide*, however, note (c), *infra*).

Notes.

(a.) The ammonium chloride used must be pure. Since 30 grms. are used to precipitate 100 c.c. of urine, and only some 30—40 m.grms. of uric acid finally weighed, it is obviously fatal to the accuracy of the process if even a very small percentage of insoluble matter is present in the salt. In some samples, sold as pure, I have found appreciable quantities of sand, and in others, an amount of fibre from the filter used in the preparation of the salt equal to 2—3 m.grms. in the 30 grms. Other mineral salts of ammonia will precipitate the urate on saturation, but none are so satisfactory as the chloride.

(b.) The presence of free ammonia greatly accelerates the separation of ammonium urate after saturation with ammonium chloride.

The addition of AmHO to urine obviously involves the separation of phosphates. But, if the samples be first saturated with the chloride, and the hydrate subsequently added, the separation of urinary phosphates is greatly modified. No gelatinous precipitate comes down, but only a small quantity of triple phosphate crystals, such as neither adds appreciably to the bulk of the urate precipitate, nor increases the difficulty of filtration (this is rendered evident if the precipitate produced by AmCl in an acid urine be first filtered off and AmHO added to the filtrate).

If, therefore, time is of special importance, AmHO may be safely added after saturation with AmCl. The urate, *plus* phosphate, may now be filtered off within ten minutes, and the uric acid liberated in the usual way.

In describing the process above, standing for two hours is recommended where AmCl is added alone. In a very large percentage of urines, however, if not in all, one hour will be found enough.

(c.) The final determination of the separated uric acid may, of course, be carried out by means of weighing on a tared filter-paper, or on a Ludwig's glass-wool filter.

Personally, however, I greatly prefer to filter the crystals through a small filter of the kind sold by Schleicher and Schüll and called by them "Gehärtete" filter-paper. From these the uric acid may be very easily washed, without loss, into a weighed glass basin. The washings are then evaporated to dryness on the water-bath, the residue dried at 110° C., and weighed.

A Volumetric Method.—Recent experience has convinced me of the utility of permanganate solutions (*vide* Sutton's "Volumetric Analysis," 4th ed., p. 89) for the accurate titration of urates; so much so that I believe uric acid, once separated, by any method, from admixture

* A Paper read before the Royal Society, June 16, 1892.

with other organic substances, may be better titrated than weighed.

At temperatures ranging round 60° C. a perfectly determinate reaction occurs, involving the instantaneous decolourisation of the permanganate; and, though oxidation continues on standing greatly beyond the limits of this reaction, a perfectly definite end-point is obtainable, giving results which will be found extremely accurate.

The uric acid separated, as above, from 100 c.c. of urine is, after washing, dissolved by warming with a minimum of Na_2CO_3 . The solution is then cooled to about 15° C., made up to 100 c.c., transferred to a flask, rapidly mixed with 20 c.c. of pure strong sulphuric acid, and then immediately titrated with one-twentieth normal potassium permanganate solution. The addition of 20 per cent of sulphuric acid produces just such a temperature as is required for the reaction. The end-point is marked by the first appearance of a permanent pink flush. On standing, the colour continues to disappear, but this slow decolourisation is in marked contrast with the instantaneous nature of the first reaction. Careful experiments with pure urates have convinced me that uric acid may be thus estimated to within less than half a milligram.

One c.c. of twentieth normal permanganate of potassium, made by dissolving 1.578 grms. of the salt in 1 litre of distilled water, is equal to 0.00375 grm. uric acid.

In the "Guy's Hospital Reports," for 1891, I have described a method in which the ammonium urate precipitate, obtained by saturation with AmCl , is directly titrated with permanganate. As this precipitate always contains a trace of pigment, the results are somewhat high, but the method will be found sufficiently accurate for clinical purposes.

Evidence as to the Accuracy of the Ammonium Chloride Separation when applied to Urine.

1. After urine has been saturated with the chloride, allowed to stand, as described, and filtered, uric acid cannot be detected by any process in the filtrate.

2. The uric acid as weighed gave the following figures on combustion. Mixed residues from actual determinations were used:—

	Found.		Theory.
	(a).	(b).	
C	35.460	35.990	35.71
H	2.561	2.590	2.381
N	32.400	31.980	33.3

The above nitrogen figures show some variation from theory, but it should be remembered that elementary analysis is a very rigorous test when applied to such unpurified products. I have never obtained figures so near to the truth from the product weighed in the Ludwig process.

3. Comparison with the standard Ludwig-Salkowski process:—

Sample.	M. grms. per 100 c.c.	
	Ludwig.	AmCl .
1.	23.0	23.0
2.	46.0	49.0
3.	55.0	57.5
4.	59.5	61.5
5.	64.0	68.0
6.	80.5	82.5
Series II.		
7.	70.5	71.0
8.	54.5	54.5
9.	40.5	39.5
10.	40.0	40.5

The experiments in Series II. will be seen to afford nearer agreement than the earlier series, carried out be-

fore the same amount of experience had been obtained. The better agreement depends partly upon the use of a purer ammonium chloride, but chiefly upon a precaution in Ludwig's method to which reference is made below.

Notes on other Processes.

Having regard to the discussion at present going on with respect to the whole question of uric acid estimation, it may not be out of place to chronicle such experience of other processes as has been gained in the course of working out the method just described.

In comparing the ammonium chloride figures with those of Ludwig's process, the experiments marked Series I. above indicated an excess by the former method equal to some 3 m.grms. from the 100 c.c. of urine. As stated above, a part of this excess was due to impurities in the ammonium chloride, but it was mainly due, I believe, to a destruction of uric acid which occurs in Ludwig's process when the silver urate is treated with the alkaline sulphhydrate. It is, of course, well known that uric acid is decomposed on heating with caustic alkalies, but it is hardly recognised with what great ease the decomposition takes place. I find that, on boiling 50 m.grms. of pure uric acid briskly for five minutes with 10 c.c. of Ludwig's sulphide solution (*vide* Neubauer and Vogel, "Analyse des Harns," p. 543), *i.e.*, the amount used to decompose the silver salt from 100 c.c. of urine, there is always an appreciable loss, sometimes amounting to 3 m.grms. It is therefore obvious that even five minutes' boiling would be fatal to the accuracy of an estimation. In Series II. above, the silver compound was thoroughly shaken up with the sulphide in the cold, and only just heated to boiling before filtration.

Mr. E. Groves, B.Sc., has recently described (*Journal of Physiology*, December, 1891) a modification of Ludwig's method which I have several times employed. Mr. Groves uses potassium iodide instead of the sulphide to decompose the silver urate. In my hands the method has always given results which are decidedly too low, owing doubtless to the action of the liberated iodine upon the uric acid in the acidified filtrate.

I have performed a large number of experiments with Haycraft's method, and have found that results obtained by its means are invariably too high, while the proportionate error undoubtedly appears to be variable. This appears to be the common experience. My own experiments, however, lend no support to the extraordinarily wide variations from the truth which some observers, especially in England, have ascribed to it. I should put the limit of error at from +10 to +15 per cent.

In conclusion, it may be claimed for the separation by means of saturation with chloride of ammonium that it yields results which are at least as accurate as those of Ludwig's method, while it is far easier to carry out, and occupies much less time.

METHODS FOR DETERMINING PHOSPHORIC ACID AND MOISTURE.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

1. *Preparation of Sample.*—The sample should be well intermixed and properly prepared and passed through a sieve having circular perforations one twenty-fifth of an inch in diameter, so that separate portions shall accurately represent the substance under examination, without loss or gain of moisture.

2. *Determination of Moisture.*—(a). In potash salts, nitrate of soda, and sulphate of ammonia heat 1 to 5 grms. at 130° C. till the weight is constant, and reckon water from the loss. (b). In all other fertilisers heat 2 grms., or if the sample is too coarse to secure uniform lots

of 2 grms. each, 5 grms., for five hours at 100° C. in a steam bath.

3. *Water-soluble Phosphoric Acid.*—Weigh out 2 grms. in a small beaker, wash by decantation four or five times with not more than from 10 to 15 c.c. of water, then rub it up in the beaker with a rubber tipped pestle to a homogeneous paste, and then wash four or five times by decantation with from 10 to 15 c.c. of water. Transfer the residue to a 9 c.m. No. 589 Schleicher and Schüll filter, and wash with water until the filtrate measures not less than 250 c.c. Mix the washings. Take an aliquot (corresponding to one-half grm.) and determine phosphoric acid as under total phosphoric acid.

4. *Citrate-insoluble Phosphoric Acid.*—Wash the residue of the treatment with water into a 200 c.c. flask with 100 c.c. of strictly neutral ammonium citrate solution of 1.09 density, prepared as hereafter directed. Cork the flask securely and place it in a water bath, the water of which stands at 65° C. (The water bath should be of such a size that the introduction of the cold flask or flasks shall not cause a reduction of the temperature of the bath of more than 2° C.) Raising the temperature as rapidly as practicable to 65° C., which is subsequently maintained, digest for thirty minutes from the instant of insertion, shaking every five minutes, filter the warm solution quickly (best with filter pump), and wash with water of about the temperature of 65°. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 c.c. of concentrated hydrochloric or nitric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 c.c., mix, pass through a dry filter, take an aliquot and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made by treating 2 grms. of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.), the residue insoluble in ammonium citrate is to be treated by one of the processes described below.

5. *Total Phosphoric Acid.*—Weigh 2 grms. and treat by one of the following methods:—(1) Evaporation with 5 c.c. magnesium nitrate, ignition, and solution in acid. This method is to be used in case of all fertilisers containing cotton-seed meal. (2) Solution in 30 c.c. concentrated nitric acid with a small quantity of hydrochloric acid. (3) Add 30 c.c. concentrated hydrochloric acid, heat, and add cautiously in small quantities at a time about 0.5 grm. of finely pulverised potassium chlorate.

Boil gently until all phosphates are dissolved and all organic matter destroyed; dilute to 200 c.c.; mix and pass through a dry filter; take 50 c.c. of filtrate; neutralise with ammonia (in case hydrochloric acid has been used as a solvent add about 15 grms. dry ammonium nitrate or its equivalent). To the hot solution for every decigram. of P_2O_5 that is present, add 50 c.c. of molybdic solution. Digest at about 65° C. for one hour, filter, and wash with water or ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution). Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 c.c. of ammonia solution of density 0.95. Let stand several hours (two hours is usually enough). Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

6. *Citrate-soluble Phosphoric Acid.*—The sum of the water-soluble and citric-insoluble subtracted from the total gives the citrate soluble.

Preparation of Reagents.

1. *To prepare Ammonium Citrate Solution.*—Mix 370 grms. of commercial citric acid with 1500 c.c. of water;

nearly neutralise with crushed commercial carbonate of ammonia; heat to expel the carbonic acid, cool, add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline) and bring to volume of two litres. Test the specific gravity, which should be 1.09 at 20° C., before using.

2. *To prepare Molybdic Solution.*—Dissolve 100 grms. of molybdic acid in 400 grms. or 417 c.c. of ammonia of specific gravity 0.96, and pour the solution thus obtained into 1500 grms. or 1250 c.c. of nitric acid of specific gravity 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment, and preserve in glass stoppered vessels.

3. *To prepare Ammonium Nitrate Solution.*—Dissolve 200 grms. of commercial ammonium nitrate in water and bring to a volume of 2 litres.

4. *To prepare Magnesia Mixture.*—Dissolve 22 grms. of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid, filter, add 280 grms. of ammonium chloride, 700 c.c. of ammonia of specific gravity 0.96, and water enough to make the volume of 2 litres. Instead of the solution of 22 grms. of calcined magnesia, 110 grms. of crystallised magnesium chloride ($MgCl_2 + 6H_2O$) may be used.

5. *Dilute Ammonia for Washing.*—One volume ammonia of specific gravity 0.96 mixed with three volumes of water, or usually one volume of concentrated ammonia with six volumes of water.

6. *Nitrate of Magnesia.*—Dissolve 320 grms. of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess, boil, filter from excess of magnesia, ferric oxide, &c., and bring to volume of 2 litres.

NOTICES OF BOOKS.

The Jeweller's Assistant in the Art of Working in Gold. A Practical Treatise for Masters and Workmen. Compiled from the Experience of nearly Thirty Years' Workshop Practice. By GEORGE E. GEE, Goldsmith and Silversmith, Author of "The Goldsmiths' Handbook," "The Silversmiths' Handbook," "The Hall-marking of Jewellery," &c., &c. London: Crosby Lockwood and Son.

MESSRS. LOCKWOOD AND SON are coming well to the front in the literature of metallurgy.

The present work is of a thoroughly practical character, and will, we feel convinced, be found exceedingly useful by the class to whom it is especially addressed; that is, not so much "beginners and young students, but advanced workmen of every department, as well as their employers." The author does not seek to enable his readers to talk about working in gold, but to practise it with success.

To what extent rule of thumb holds sway even in the delicate art of the gold-worker may be judged from an incident narrated on pp. 17 and 18. We cannot help fearing that the master jeweller who figures there is the type of a class too numerous in all the arts. The country in which such characters are most numerous and most obstinate is precisely the one which will take the lowest rank in the industries of the future.

The work treats in successive chapters of the chemical and physical properties of gold, of the precipitation of gold in waste solutions, of the different colours of gold, of mixing and melting gold, of dry-colouring and wet-colouring gold, melting and casting gold, electro-gilding, other modes of gilding, practical manipulations, mixing alloys, useful imitation alloys, hints and helps, collecting

and refining, sundry gold alloys, choice recipes, and gold values and alloys.

Anyone who doubts whether this work was needed will be edified by reading certain passages in Chapter V. on "defective and wrong information," and "erroneous statements." In some departments a judicious well-read compiler may produce a useful treatise, but this is not the case in technology.

An Appeal to the Canadian Institute on the Rectification of Parliament. By SANDFORD FLEMING, C.M.G., LL.D., &c. Toronto: The Copp, Clark Company, Limited, 1892.

WHATEVER may be the views of the Canadian Institute, we, at any rate, must dismiss Mr. Sandford Fleming's "appeal" as being distinctly outside our jurisdiction.

Annual Archaeological Report and Canadian Institute (Session 1891): being an Appendix to the Report of the Minister of Education, Ontario. Printed by order of the Legislative Assembly. Toronto: Warwick and Sons, 1891.

THIS report is certainly scientific, and so far highly interesting, but it is entirely confined to archæology, anthropology, and ethnology. The introduction is well worth reading.

A Systematic Course of Qualitative Chemical Analysis of Inorganic Substances. With Tests for the more important Metals and Acids. (For the Use of Students of Analytical Chemistry). Compiled by C. F. JURITZ, M.A., Fellow of the University of the Cape of Good Hope, Analytical Chemist; Senior Analyst, Department of Agriculture, Cape Colony. Cape Town and Johannesburg: J. C. Jutta and Co.

THIS "systematic course" is compact and correct in its indications, but we can scarcely enter into the author's views when he writes in his preface: "In default of the existence of a suitable course of qualitative analysis in the English language, I found it necessary while a student at the South African College to translate for my own use, from the German, certain portions of the late Professor Heintz's work on qualitative analytical chemistry." We should have thought the only difficulty would be to make a selection of any one book out of so many, all correct in their teachings, and which earned the approval of the profession. For us to recommend any one manual out of the crowd would be scarcely just either to the authors or to the publishers of the others.

We wish Mr. Juritz could have seen his way to use the nomenclature adopted by the Chemical Society.

Development of Gases.—Neumann (*Journ. fur Prakt. Chemie*).—The author obtains continuous currents of hydrochloric acid gas from carnallite and concentrated sulphuric acid; gaseous ammonia from solid potassium hydroxide and aqueous ammonia; nitrogen from chloride of lime and ammonia.

Methods Proposed for Determining Paratoluidine in Commercial Toluidines.—F. F. Raabe (*Chemiker Zeitung*).—After criticising previous methods the author lays down the following process, by means of which he has obtained good and expeditious results. He adds to a commercial sample so much weighed paratoluidine as to yield a mixture the congealing-point of which can be determined. A thermometer with a scale extending from 30°–50°, and graduated in twentieths of a degree, shows differences of 0.2 per cent of paratoluidine. As standards he prepares solutions containing, respectively, 82.5, 83, 83.5, 84, 84.5, and 85 paratoluidine, and determines their congealing-points. It is recommended always to work with equal quantities. The toluidines to be used in this determination must be anhydrous.

CORRESPONDENCE.

WANTED,—CONSISTENCY.

To the Editor of the Chemical News.

SIR,—It is with regret that I see that your correspondent "Ous" thinks me wanting in consistency in using the terms sodic and magnesian sulphates. As I can hardly make out from his letter whether he approves of my nomenclature or not, I had better reply by stating my reasons for using the terms.

I regard the words sodic and magnesian as adjectives. Just as the name acid of sulphur was changed into sulphuric acid, so chloride of sodium has been altered into sodic chloride, or that chloride which is sodic. The name sodium chloride seems to me incorrect, and not analogous to the German chlornatrium. Up to the present (happily or unhappily?) we do not construct compound substantives, or we should translate chlornatrium into chlorine sodium or sodium chlorine, and certainly not sodium chloride.

If sodic chloride is inadmissible,—so must of necessity be hydrochloric acid,—"Ous" would probably take refuge in the name hydrogen chloride. On one point, however, I think we should agree, namely, in condemning the use of loose expressions that we sometimes hear from students, such as "dissolving a substance in hydrochloric."

I do not think that the terms sodic and magnesian sulphates at all imply the existence of sodious and magnesian compounds. An equal objection might be taken to my using the expressions "an enormous house" or "a terrific storm," as necessarily implying "an enormic house" or a "terrific" or "perterrific" storm.—I am, &c.,

HERBERT MCLEOD.

Scarborough, Aug. 22, 1892.

A CURIOUS POINT IN THE HISTORY OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—One of my friends, who is the owner of a bound copy of the CHEMICAL NEWS for the year 1868, was good enough to allow me to refer to the report of the Anniversary Meeting of the Chemical Society, held March 30, 1868, and in your report I find the missing list of officers and council elected at the meeting.

As I mentioned, there is a curious interest attached to that list, and the circumstance that it is to be found in your pages and not in the volume of the *Journal of the Chemical Society* is very singular. The omission forms one of a series.

On June 18, 1868, I read a paper to the Chemical Society, the title of which is to be found in the Society's *Journal*, but the paper itself will be sought for in vain in its pages. An abstract of it, and also a curious discussion on the paper, is to be met with in the CHEMICAL NEWS.—I am, &c.,

J. ALFRED WANKLYN.

New Malden, Surrey,
Aug. 23, 1892.

ESTIMATION OF CAOUTCHOUC.

To the Editor of the Chemical News.

SIR,—With regard to the remarks made by your correspondent Mr. Carter Bell in the CHEMICAL NEWS (vol. lxi., p. 84), I may say that there was no "rubber substitute" present in the rubber mat in question. Although I will admit that the presence of old rubber is very probable, as suggested by your correspondent Mr. J. K.

Burridge at page 97. A good price was paid for the mat, and it is well known that mats are made with pure caoutchouc mixed with old rubber, the total caoutchouc in the composition amounting to over 50 per cent. The following is an analysis of such a mat as made by M. Guibal:—

Caoutchouc	40	} = 55 per cent.
Chippings of vulcanised rubber	15	
Litharge	35	
Chalk	8	
Sulphur	2	
	100	

The writer is at present engaged in research work on rubber and gutta-percha goods, and hopes to be able to publish results later on.

Ap[ro]pos of gutta-percha, I recently had a sample of gutta-percha dielectric submitted to me for analysis, supplied to specification as "*best gutta-percha*." From this sample I succeeded in dissolving out by boiling absolute alcohol 47 per cent of resin. According to M. Payen, ordinary gutta-percha should not give up more than 22 per cent of resinous matter to boiling alcohol—this amount, of course, being naturally present in the substance. From a sample of raw gutta-percha obtained from a leading firm of manufacturers in London I extracted 30 per cent of resinous matter. No doubt the amount soluble in alcohol varies in samples obtained from different countries.

I should be pleased to hear from any chemist who has estimated the maximum proportion of resin, &c., dissolved by raw gutta-percha obtained from various sources.—I am, &c.,

H. JOSHUA PHILLIPS, F.I.C.

G.E.Ry. Laboratory, Stratford,
London, August 22, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 11.

The Determination of Nitrogen in Nitrates, Nitric Ethers, and Nitro-Derivatives, by Kjeldahl's Method.—L. Chenel.—The author's analytical results prove that Kjeldahl's method with Jodlbauer's modification facilitates the analysis of many compounds which require the method of Dumas. As it consists of an interrupted series of three or four very simple operations, it has the advantage over the Dumas process of being less burdensome, and of not requiring a prolonged and sustained attention.

New Derivatives of Amethylcamphonitroketone.—P. Cazeneuve.—Already inserted.

Tinctorial Properties of Methylcamphonitroketone and its Auxochromic Grouping.—P. Cazeneuve.—Already inserted.

New Bacillus found in Rain-Water.—Dr. A. B. Griffiths.—Already inserted.

The Preservation of Solutions of Sulphuretted Hydrogen.—MM. Salazar and Neumann.—The authors draw from their experiments the conclusions that solutions of H₂S keep better the smaller the quantity of air to which they are exposed. As regards preservation there is great advantage in dissolving the H₂S in Lepage's mixture in preference to water. The oxidation of dissolved H₂S is more rapid in light than in darkness.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xix., No. 1.

The Principles of Modern Agriculture.—J. Pyro.—The author admits that certain plants are capable of fixing atmospheric nitrogen. He quotes Palissy as having many years ago insisted on the restoration to the soil of all the waste products of vegetable and animal life. He criticises Ville's "sideration" as having been long known and practised, forgetting that at present a vast part of the solar energy which actually reaches our earth is allowed to be wasted.

Volumetric Determination of Mercury.—M. Rod. Namias (*Gazzetta Chimica Italiana*).—This paper will be inserted in full.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1710.

ON THE IODIDES OF SULPHUR.*

By Prof. HERBERT McLEOD, F.R.S.

AN iodide of sulphur, SI_6 , isomorphous with iodine, was prepared by Landolt and measured crystallographically by Vom Rath (*Poggendorff's Annalen*, cx., 116). It was made by allowing a solution of iodine and sulphur in carbonic disulphide to evaporate spontaneously. As the existence of this compound has been adduced as a proof of the hexad character of sulphur, it seemed advisable to investigate its properties.

Some of the substance was prepared by the process mentioned, and in order to separate it from any admixture of iodine, it was placed in a tube which was afterwards exhausted by the Sprengel pump and sealed. One end of the tube was then surrounded by muslin kept wet with water by means of a piece of cotton wick; iodine volatilised, at first rapidly but afterwards more slowly. After the lapse of three months a residue was left at the end of the tube which, on analysis, was found to contain 98·5 per cent of sulphur.

Another quantity was dissolved in carbon disulphide and the solution allowed to evaporate; as crystals were formed the liquid was poured off and the crystals washed with carbonic disulphide. In this manner five crops of crystals were obtained, none of which contained more than half a per cent of sulphur; the residue left on allowing the mother-liquor to evaporate contained 56 per cent of sulphur.

The iodine is entirely removed from the substance by digesting it in a solution of potassic iodide.

When some of the powdered substance is exposed to the air in a shallow layer, the iodine all volatilises, leaving a residue of sulphur.

When acted on by a solution of sodic hydrate, a residue of sulphur is left, and the solution gives very little precipitate with baric chloride after acidifying with hydrochloric acid.

The properties of the substance seem to indicate that it is a mechanical mixture of iodine and sulphur and not a chemical compound.

Some experiments were then made with the iodide of sulphur, S_2I_2 , described by Guthrie. This was prepared by mixing chloride of sulphur, S_2Cl_2 , with ethylic iodide, and allowing the mixture to remain in a sealed tube for four days. Black crystals were then found in the tube. On opening the latter a large quantity of the vapour of ethylic chloride escaped.

The crystals were removed from the tube and powdered. On heating a portion in a test-tube it fused at a temperature a little above the boiling-point of water.

Some of the substance *in vacuo* gave off iodine, leaving a light coloured residue. Some of the substance dissolved in sulphide of carbon was crystallised fractionally; the first crop contained 0·38 per cent of sulphur; the second 0·31; the third 1·07; and the fourth 34·78. On allowing the mother-liquor to evaporate, the residue contained 76·32 per cent of sulphur.

When acted on by a solution of sodic hydrate the iodine is removed and all the sulphur remains behind, the solution giving no precipitate with baric chloride after adding hydrochloric acid. It is usually stated in text-books that the compound undergoes a decomposition similar to that of the chloride of sulphur, forming an iodide and a sulphite or thiosulphate, with separation of sulphur.

The fusing-point being lower than those of iodine and sulphur would indicate that some chemical action takes place when the elements are mixed together, but its properties more resemble those of a non-metallic alloy than of a definite chemical compound.

THE HALOGEN ADDITION PRODUCTS OF SALTS OF ORGANIC BASES.*

By LEONARD DOBBIN, Ph.D., and JAMES WALKER, Ph.D., D.Sc.

DOBBIN and Masson prepared well-defined compounds, NMe_4IBr_2 , NMe_4ICl_2 , SMe_2IBr_2 , and SMe_2ICl_2 , by the action of bromine and of chlorine on the iodides of tetramethylammonium and of trimethylsulphine. The authors have now prepared analogous compounds, $(C_5H_5N)CH_3IBr_2$ (m.p. 63°) and—

$(C_5H_5N)CH_3ICl_2$ (m.p. 88°),

from methylpyridium iodide. These trihalogen compounds are not equally stable on exposure to moist air, the dibromiodides being more stable than the dichloriodides, and the methylpyridium derivatives being much more stable than the corresponding trimethylsulphine derivatives, with the tetramethylammonium compounds in an intermediate position. In order to test their stability with regard to boiling alcohol, determinations of the elevation of the boiling-point of their alcoholic solutions were made by means of Beckmann's apparatus, and from these observations the molecular weights were calculated with the following results:—

	Dibromiodides.		Dichloriodides.	
	Theory.	Found.	Theory.	Found.
Methylpyridium . . .	381	386	292	276
Tetramethylammonium . .	361	353	272	239
Trimethylsulphine . . .	358	293	269	208

These numbers show that the dibromiodides of methylpyridium and tetramethylammonium are not appreciably attacked by boiling alcohol; that methylpyridium dichloriodide is slightly attacked; and that the other compounds are all decomposed to a marked extent by five to fifteen minutes' boiling. If the boiling is prolonged the molecular weights of the dichloriodides sink continually, indicating increased decomposition, which may also be observed from the change of colour of the solutions. There is thus a continuous series of analogous compounds ranging from methylpyridium dibromiodide, which is perfectly stable in boiling alcohol, down to trimethylsulphine trichloriodide, which is at once decomposed by cold alcohol, being only stable in an atmosphere of dry chlorine. The first mentioned substance has all the characters of an ordinary "atomic compound"; the second those of a so-called "molecular compound"; yet these substances are only the extreme terms of a continuous and perfectly uniform series, so that atomic and molecular compounds must be of the same order.

WATER ANALYSIS.

(No. II.)

By J. ALFRED WANKLYN.

ALTHOUGH the first detailed and authoritative publication of Frankland's "Water Analysis" took place in the *Journal of the Chemical Society* for the year 1868, the essential features of the process were disclosed before the advent of Wanklyn, Chapman, and Smith's ammonia-process; and it is historically true that our process was

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

produced under a lively sense of the great difficulty and utter futility of the Frankland process. Both Chapman and myself had had personal experience of the working of one of the initial forms of Frankland's process, and that experience formed an important factor in determining the nature of the ammonia-process. Not only did we recognise that it was absolutely impossible for Frankland's method to measure the carbon and nitrogen existing in drinking waters, but we went much further and opened our eyes so as to see that a knowledge of the total organic carbon and nitrogen in drinking water would not supply the datum required for sanitary purposes.

It is only right to remark that the belief in the necessary utility of the organic carbon and nitrogen determination was by no means confined to Chapman and myself, but was shared by leading authorities a quarter of a century ago; and that very careful and trustworthy chemist, Dr. William Allen Miller, expressed himself very strongly as to the uselessness of such determinations. A consideration which led chemists of a former generation to decline to attempt a Frankland measurement of organic carbon was that such a measurement (even if valid), would lump together the end products of vegetable and animal disintegration with the fresh intact vegetable and animal products. The general vegetable products, cellulose, starch, sugar, and gluten, enter into many drinking waters and presently ferment, yielding carbonates, nitrates, acetates, lactates, succinates, and other products. Now traces of acetates, lactates, benzoates, succinates, and traces of hydrocarbons, are neither harmful nor indicative of danger, and a total organic carbon determination would register them as if they were dangerous.

In striking out a new line of water analysis we resolved not to lump together all the organic matter,—not to confound that which was harmless and not indicative of danger with that which was either harmful or indicative of danger. We reflected that the harmful or dangerous organic matter must be either itself albuminous or else a complex nitrogenous derivative of albumen. Water destitute of such materials would be perfectly safe; water containing much of such materials we recognised as either harmful or risky.

Our measurement of albuminous substances, whether of animal or vegetable origin, was founded on the observation that egg albumen or gluten yields about one-tenth of its weight of ammonia when operated upon under certain sharply defined conditions. Ammonia obtained from a drinking water under these conditions I named albumenoid ammonia. The quantity of ammonia obtained under these conditions is the measure of the albuminous substance in the water. It is the measure of the potential albumen. If all the complex nitrogenous organic matter consisted of egg albumen or gluten the actual weight of it would be ten times the weight of the albumenoid ammonia; if it existed in other states of combination other weights of nitrogenous substance would correspond to a given weight of albumenoid ammonia. There is no reason to expect that the real absolute weights of the dry nitrogenous substances would be at all a better numerical expression for the degree of contamination than the quantities of albumenoid ammonia directly measured and recorded.

In the whole history of chemical analysis there is hardly any process which has been subjected to more rigid practical investigation. It is now twenty-five years old, and its appreciation has had no other source than its own trustworthiness and especial adaption to the purposes for which it was designed. How many persons at present employ our process in different parts of the world is to be reckoned at many thousands, and nearly ten thousand copies of our work on water analysis are in the hands of the public. Under these circumstances any endeavour to suppress the ammonia-process is likely to prove as futile as an attempt to stop the rising tides. But we are threatened

with a visitation of cholera, and the perverse action of a Government department might for the moment deprive the nation of the advantage of a correct discrimination of the different kinds of drinking water, which at times like the present means life or death to individuals.

Whether or not there is risk that a given well is cholera laden is a question to which the ammonia-process can give a correct answer; it remains to be seen whether the opportunity will be given to that process.

New Malden, Surrey,
Aug. 30, 1892.

METHODS OF ANALYSIS OF FERMENTED LIQUORS.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1890-91.

I. *Specific Gravity*.—This determination is made with a pycnometer, or a Westphal balance controlled by a pycnometer. Temperature 25° C.

II. *Alcohol*.—One hundred c.c. of wine at 25° C. distilled (preferably in glass) give + c.c. alcohol.

III. *Extract*.—Fifty c.c. of wine (at 25° C.), in case of sweet wines a less amount, are evaporated in a platinum dish on the water-bath to the proper consistency, and then dried in a drying oven at 100° C. to constant loss of weight. Constant loss of weight is assumed when three weighings with equal intervals between the first and second and second and third give equal differences between the successive weighings. Weighings are to be made at intervals of fifteen minutes.

(*Note on the Extract Determination*.—So far as I am aware no satisfactory method has been given for the determination of the extract of wine. I think that the method of the Bavarian chemists is on the whole the best. As the object is for purpose of comparison with some standard, we cannot do better, I think, than to follow the standard most generally adopted. I have in mind when the new Chemical Laboratory of the University of California is fitted up to make some experiments on the determination of this extract in a vacuum at a moderate temperature. I should modify somewhat the method of Gautier. However, until some better method has been established, I believe the method given will be most satisfactory).

IV. *Acidity* (total acid constituents of the wine expressed as tartaric acid).—If carbonic acid is present, expel by shaking. Titrate with dilute alkali solution. The neutral point is determined by adding a drop of solution to delicate litmus-paper.

V. *Volatile Acids* (expressed as acetic acid).—Distil in a current of steam, and titrate the carefully condensed distillate with standard alkali (decinormal).

VI. *Glycerin*.—(1) This is determined in dry wines as follows:—The alcohol is driven off from 100 c.c. wine, lime or magnesia added, and the same evaporated to dryness. The residue is boiled with 90 per cent alcohol, filtered, and the filtrate evaporated to dryness. This residue is dissolved in 10 to 20 c.c. alcohol, 15 to 30 c.c. ether added, and the mixture allowed to stand until it is clear. It is then decanted from the sticky precipitate into a glass-stoppered weighing bottle, evaporated to constant loss of weight, and weighed.

(2) The following method is employed for sweet wines:—One hundred c.c. wine are measured into a porcelain dish and evaporated on the water-bath to a syrupy consistence, mixed with 100 to 150 c.c. absolute alcohol, poured into a flask, ether added in the proportion of 1½ volumes to each volume of alcohol used, the flask well shaken, and allowed to stand until the liquid becomes clear. This is then poured off, and the residue again treated with a mixture of alcohol and ether. The liquids are mixed, the alcohol and ether driven off, the residue dissolved in water, and treated as in (1).

(3) In all glycerin determinations it is necessary to take into consideration the loss of glycerin due to its volatility with water and alcohol vapour, and accordingly to add to the glycerin found 0.100 grm. for each 100 c.c. of liquid evaporated.

(4) It is necessary to test the glycerin from sweet wines for sugar, and if any is present it must be estimated by Soxhlet's or Knapp's method, and its weight subtracted from that of the glycerin.

VII. *Sugar*.—This is to be determined by Soxhlet's or Knapp's method. The presence of unfermented cane-sugar is to be shown by inversion, &c.

Polarisation.—(1) The wine is decolourised with plumbic subacetate.

(2) A slight excess of sodic carbonate is added to the filtrate from (1). 2 c.c. of a solution of plumbic subacetate are added to 40 c.c. white wine, and 5 c.c. to 40 c.c. red wine; the solution is filtered, and 1 c.c. of a saturated solution of sodic carbonate added to 21.0 or 22.5 c.c. of the filtrate.

(3) The kind of apparatus used and the length of the tube are to be given, and results estimated in equivalents of Wild's polaristrobometer with 200 m.m. tubes.

(4) All samples rotating more than 0.5 degree to the right (in 220 m.m. tubes, after treating as above), and showing no change, or but little change, in their rotatory power after inversion, are to be considered as containing unfermented glucose (starch sugar) residue.

(5) Rotatory power of less than 0.3 degree to the right shows that impure glucose has not been added.

(6) Wines rotating between 0.3 degree and 0.5 degree to the right must be treated by the alcohol method.

(7) Wines rotating strongly to the left must be fermented, and their optical properties then examined.

VIII. *Tannin*.—Determine with Neubauer's permanent method.

IX. *Potassic Bitartrate*.—The determination of potassic bitartrate as such is to be omitted.

X. *Tartaric, Malic, and Succinic Acids*.—(1) According to Schmidt and Hiepe's method.

(2) Determination of tartaric acid according to the modified Berthelot-Fleury method.

(3) If the addition of 1 grm. finely powdered tartaric acid to 100 grms. wine produces no precipitate of potassic bitartrate, the modified Berthelot-Fleury method must be employed to determine free tartaric acid.

XI. *Colouring Matter*.—(1) Only aniline dyes are to be looked for.

(2) Special attention is to be paid to the spectroscopic behaviour of rosaniline dyes as obtained by shaking wines with amylic alcohol before and after saturation with ammonia.

XII. *Inorganic Matter (ash)*.—Burn in ordinary manner in flat platinum dish at as low a heat as possible; repeated moistening, drying, and heating to redness are advisable to get rid of all organic substances.

XIII. *Citric Acid*.—Presence to be shown by a qualitative test, as baric citrate.

XIV. *Sulphuric Acid*.—To be determined in the wine after adding hydrochloric acid.

XV. *Chlorine*.—To be determined in the nitric acid solution of the burnt residue by Volhard's method.

XVI. *Lime, Magnesia, and Phosphoric Acid*.—These are determined in the ash fused with sodic hydrate and potassic nitrate, the phosphoric acid by the molybdenum method.

XVII. *Potash*.—Either in the wine ash, as the platinum double salt, or in the wine itself, by Kayser's method.

XVIII. *Gums*.—Presence shown by precipitation by alcohol; 4 c.c. wine and 10 c.c. 96 per cent alcohol are mixed. If gum arabic has been added, a lumpy, thick, stringy precipitate is produced; whereas pure wine becomes at first opalescent and then flocculent.

XIX. *Sulphurous Acid*.—One hundred c.c. of wine are distilled in a current of carbonic acid after the addition of phosphoric acid. The distillate carefully condensed is

oxidised with bromine, and the amount of H_2SO_4 determined.

Abnormal Constituents of Wines.

Mannite.—When present in any considerable quantity it can be detected by simply allowing the wine (a few drops will be sufficient) to evaporate spontaneously upon a glass slide or plate. The mannite will crystallise in a characteristic stellated form, which can be recognised at a glance. It should be allowed to stand twenty-four to forty-eight hours. When the quantity is small, extract the residue evaporated nearly or quite to dryness with boiling 80 per cent alcohol. Evaporate this extract to dryness, and extract with 95 per cent boiling alcohol; the mannite, if present in any quantity, will separate out in part upon cooling. If allowed to evaporate spontaneously the characteristic stellated crystals can be obtained.

Lactic Acid.—This will be found in the alcohol ether extract of evaporated residue, and can be recognised by usual tests. It may be determined by titration with standard alkali. It may be necessary to take larger quantities of the wine for this investigation.

In diseased wines butyric acid may be tested for in the portion of volatile acid.

A QUICK METHOD OF PREPARING SILICON, ALUMINIUM, AND OTHER CHLORIDES IN QUANTITY.

By H. N. WARREN, Research Analyst.

FOR the preparation of silicon chloride a sample of silicon-eisen containing about 15 per cent silicon was selected, introduced into a deep clay retort provided with a tubulure, and connected with an apparatus evolving dry chlorine gas, the pipe conveying the gas passing nearly to the bottom of the retort, while the stem of the same was connected to a suitable adapter, maintained at the required heat by the aid of hot water, and intended to condense and retain the volatile ferric chloride, which would naturally accompany the silicon chloride; the termination of the adapter being further connected with a suitable refrigerator containing a mixture of salt and ice in order to retain the volatile tetrachloride of silicon, SiCl_4 .

The retort and its contents being now raised to redness by the aid of ignited charcoal, and the chlorine then allowed to play into the same, almost immediately the dense greenish yellow vapour of gaseous ferric chloride is observed traversing the space within the adapter, and speedily condensing into the form of brilliant plates upon the walls of the same; while, at the more remote end, is observed the condensation of the silicon chloride, not unfrequently contaminated by the presence of small quantities of ferric chloride, which, however, may be entirely removed by subjecting the latter to distillation.

Further advantages may be obtained by substituting for the chlorine gaseous hydric chloride. This gas, on account of its forming with the iron a ferrous salt, practically non-volatile at ordinary temperatures, is itself retained in the retort, and at the termination of the reaction may be detached by pouring the same while in the liquid form, while, at the same time, a further charge may be introduced. Thus, by acting upon the element silicon at an elevated temperature by means of gaseous hydric chloride, a still more volatile liquid chloride of silicon is obtainable, corresponding to a hydro-trichloride, and represented by the formula of SiHCl_3 . In this instance, however, the formation of silicon itself, which in the elementary form is by no means easy as regards its preparation, is absolutely necessary; but, by substituting for the same a sample of silicon-eisen containing a rich percentage of silicon, the corresponding chloride may be as readily prepared as in the former instance.

For the preparation of aluminium chloride an alloy of

iron and aluminium containing about 10 per cent of the latter was selected, and the chloride thus obtained purified by intimately mixing it with iron borings and distilling the same; or the pulverised regulus mixed with common salt previous to exposing it to the action of chlorine yields as a sublimate aluminium-sodium-chloride.

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ON THE DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

(Continued from p. 105).

POTASSIUM chromate and bichromate solutions show no irregularities like those of the chromic salts. Potassium chromate solution does not appear to decrease in colour in the least even at 100 litres dilution. Chromic oxide, on the other hand, shows great decrease, the colour effect at 100 litres being less than half that of the normal solution. This is probably owing to the colour of the concentrated solution, being in great part due to the presence of excess of chromium trioxide molecules dissolved in the H_2CrO_4 existing in solution, and which as dilution proceeds, are gradually converted into H_2CrO_4 , with decrease of colour effect of the solution. Thus it is known that when sulphuric acid is added to a solution of potassium bichromate it becomes considerably darkened in colour, and this can only be due to the presence of chromium trioxide existing as such in the solution. If the colour produced by viewing solutions of potassium chromate and chromium trioxide in separate tubes, placed one on top of the other, be compared with the colour of a solution of potassium bichromate of equivalent strength, it is found that the bichromate solution is more than four times as dark in colour. It is thus evident that potassium bichromate, even in solution, forms a distinct and stable compound, and does not decompose into K_2CrO_4 and CrO_3 .

Ferric chloride solutions gave peculiar results. This was due to the presence, in the ferric chloride solutions, of free iron sesquioxide, the formation of which was probably due rather to the action of the mass of water present than to the electrolytic dissociation of the ferric chloride.

The acid ferric chloride solutions contained six equivalents of free hydrochloric acid to the normal and 5 litre solutions, and twelve equivalents to the 10 and 100 litre solutions. It was not possible to colorimetrically compare the 1 and 5 litre solutions, as the 1 litre solution was a yellowish brown colour, and the 5 litre solution a bright yellow. The acid ferric chloride solution is remarkable in that it shows a far greater colour decrease on dilution than any other salt examined. In solution ferric chloride is evidently an unstable salt, both in the ordinary sense of the word and in the electrolytic dissociation sense.

Ferric acetate proved to be a very unstable salt when no free acetic acid was present, it decomposing spontaneously with precipitation of the basic acetate. 2 c.c. of free acetic acid was therefore added to 100 c.c. of the solution. Like ferric chloride, the solution increases in colour effect on dilution, and, as will be shown later, probably from the same reason. A stronger solution than the decinormal could not be examined, as it was so dark in colour. The two separate series of determinations made with solutions of ferric citrate, and of ferric citrate containing five molecules of free citric acid, showed no difference in dissociation values, but both showed great increase of colour on dilution. Ferric citrate free from

citric acid was obtained by decomposing barium citrate with ferric sulphate.

Ferric oxalate solution was prepared by boiling precipitated ferric oxalate with oxalic acid solution till no more would dissolve and filtering off the solution. In its behaviour on dilution the solution of this salt resembles acid ferric chloride solution, though it does not dissociate to so great an extent. Ferric ammonium citrate solution behaves quite differently, however, and does not on dilution appear to change at all in colour effect. Ferric tartrate solution, containing no free tartaric acid, was prepared by decomposing barium tartrate with ferric sulphate. It showed a greater increase of colour effect on dilution than the solution of any other salt examined. This was due to the same cause that produced the great increase of colour effect with solutions of ferric chloride and acetate, *i.e.*, the formation in solution of ferric oxide. The quantity of iron in these ferric salts was determined by evaporating down and igniting some of the salt in a platinum crucible, moistening with nitric acid, again igniting, and weighing as Fe_2O_3 .

Ferrous citrate solution was prepared by decomposing barium citrate with ferrous sulphate. It decreases greatly in colour effect on dilution.

Potassium ferrocyanide and ferricyanide solutions decrease in colour effect to a moderate extent on dilution, whilst potassium permanganate only shows traces of decrease at extreme dilutions. The values given for this salt are for solutions a hundred times more dilute than the dilutions they are placed under, for more concentrated solutions were too dark for colour comparison. The slight increase in colour effect at dilutions of 1000 litres and 10,000 litres are rather too great for experimental error.

The general conclusions to be drawn from the changes in colour attending the dilution of solutions of coloured salts are, that almost all salt solutions show a decrease in colour effect; but a few, notably several organic salts of iron, show a considerable increase in colour. It is difficult to find an adequate explanation for these changes in colour effect, except on the ground of electrolytic dissociation. Of the salts examined which do not decrease in colour effect on dilution, the chromium salts are the most notable instances. Potassium chromate was not, perhaps, examined at a sufficient dilution, for potassium permanganate, a salt to which it bears some sort of resemblance, only showed a decrease in colour effect at a dilution of 50,000 litres. The ferric salts are the chief exceptions, but the cause of such behaviour on the part of ferric chloride has already been explained. It is thus seen that with a few doubtful exceptions coloured salts, by the decrease in colour effect of their solutions on dilution, appear to undergo partial dissociation.

The reciprocals of these colour effect values for different salts should be proportional to their electrical conductivities at the same dilutions. Not many of the salts examined here appear to have been examined electrically, but as a general rule it is evident that the colour effects of salts do not decrease to so great an extent as the electrical conductivities increase. Thus most salts on dilution from 1 to 1000 litres have their conductivities more than doubled. It must be remembered, however, that it has not been shown whether or no the dissociated ions themselves produce any colour effect in a solution. From the fact that while most ferric salt solutions are deeply coloured, and that of the sulphate is nearly colourless, it does not seem to be essential that a base forming some salts coloured should form all. Also most ferrous salts form only slightly coloured solutions. Again, cupric sulphate in the anhydrous state is a white powder. On the other hand, in that all cupric, cobalt, nickel, chromium, and uranium salts form coloured solutions, it would seem that the formation of such coloured solutions is so essential a property of salts of certain metals that it cannot be considered impossible that this property should extend even to the ions, though it is far from probable. It is

not possible therefore to speak with certainty either way. The changes in colour effect of solutions of salts on dilution are evidently due to more than one cause. As will be shown, the formation of hydrates will account for them in part. They cannot be wholly accounted for in this way, however. Electrolytic dissociation seems to be the only ground left on which an explanation is possible.

(To be continued.)

NOTES UPON THE ESTIMATION OF CHLORINE IN ELECTROLYSED SOLUTIONS.

By L. M. NORTON, Ph.D.

THE numerous experiments made during the last few years upon the production of chlorine, hypochlorites, and chlorates by the electrolysis of solutions of chlorides, have brought into the hands of analysts solutions containing chlorine in several combinations.

It has been found that rapid volumetric methods for the determination of the combinations in which the chlorine existed were a necessity where such solutions were to be frequently tested, and the writer thinks a description of the methods he has employed, while they contain little that is new, may be of interest to chemists who deal with similar problems.

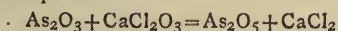
By the direct electrolysis of aqueous solutions containing sodium chloride at ordinary temperatures, solutions are obtained which contain sodium chloride, sodium hypochlorite, and sodium chlorate, and this general action is undoubtedly true in regard to other chlorides. A most careful examination has failed to show the presence of sodium chlorite in solutions thus prepared. If, however, the temperature is raised to 50–55° C. (Rigaut, "*La Lumière électrique*, xl., 102) the solution contains mainly sodium chloride and sodium chlorate.

Such solutions may be very conveniently examined by the methods described below.

Estimation of Chlorine combined as Hypochlorite.

A quantity, 25 c.c. for example, of the solution is measured out and titrated in the ordinary manner with a sodium arsenite solution of known strength. The solution after the titration must be preserved for the determination of the chloride present.

From the equation—



the quantity of chlorine combined as hypochlorite may be calculated.

Estimation of Chlorine combined as Chloride.

The portion of the original solution which has been titrated with sodium arsenite is now conveniently made up to a known volume and an aliquot part is taken. To this part a solution of pure potassium chromate is added, and the solution then titrated with silver nitrate of known strength. The presence of arsenic compounds does not interfere with this titration in any way; in fact, sodium arsenite may be used as an indicator in the place of potassium chromate, and equally good results may be thus obtained.

The figures furnished by the titration with silver solution give the chlorine present as chloride and hypochlorite together in the original liquid. By subtracting the chlorine combined as hypochlorite from the chlorine shown by the titration with silver solution, the chlorine present per c.c. as chloride is readily obtained.

Estimation of the Total Chlorine.

It might seem at first thought that the total chlorine could be obtained by the titration of the original solution which had been electrolysed; but this is not the case, a

during the electrolysis of a chloride solution there is a decrease in its volume caused by the rise in temperature due to the current, so that the contents per c.c. of the solution before and after electrolysis are not comparable, unless, in the latter case, the solution is carefully brought to its original volume by the addition of water. A further error is unavoidably introduced by a loss of chlorine due to its escape directly into the air during the electrolysis, a loss which the writer has always observed in the various forms of apparatus which he has used.

As the solutions under discussion contain chlorine in two oxidised forms, as well as in the form of chloride, it is of course evident that for the determination of the total chlorine the simplest method will be the reduction of the oxidised chlorine compounds to the form of chloride, and a subsequent titration with silver solution. Various reducing agents have been recommended from time to time for the reduction of chlorates to chlorides with a view to the subsequent titration of the chlorides with silver solution. After many experiments, the writer has found that the most satisfactory agent for this reduction is a saturated aqueous solution of sulphurous acid. This was suggested by Rose ("*Handbuch der Analytischen Chemie*," ii., 613, Leipzig, 1871), and lately Engel (Silva, "*Traité d'Analyse Chimique*," 151, Paris, 1891) has called attention to its possible use in this connection. Chlorates are completely reduced to chlorides by boiling for a few moments with an excess of an aqueous solution of sulphurous acid, with or without the addition of nitric or sulphuric acid. Thus the following figures were obtained in the analysis of a sample of commercial chlorate of potash by reduction with sulphurous acid solution, after acidifying strongly with nitric acid, boiling off the excess of sulphurous acid, followed by titration with silver solution in the manner to be mentioned below:—

	Theory for pure KClO ₃ . Per cent.	Found. Per cent.
Chlorine	28.93	28.70, 28.82, 28.82, 28.79

As during the reduction free acid is formed in the chlorate solution, even if it is not added at the beginning, the use of potassium chromate as an indicator, together with direct titration with silver nitrate solution, failed to give satisfactory results. The figures obtained, however, were entirely satisfactory if the reduced solution was treated with an excess of silver nitrate solution of known strength, ferric alum added as an indicator, and the excess of silver nitrate determined by titration with ammonium sulphocyanate solution in the manner recommended by Volhard (*Annalen der Chemie*, etc., 1).

The total chlorine being thus obtained, the amount present as chlorate per c.c. is easily found by subtracting from the total quantity the amount previously ascertained to be present in the form of chloride and hypochlorite.

It is also practicable to determine the hypochlorite by means of an arsenite solution, the chlorine present as chloride and hypochlorite together by means of silver solution as given above, and the hypochlorite and chlorate by allowing them to act upon potassium iodide in the way ordinarily described in the handbooks; and from the data thus obtained the amount of chlorine present in each form can then be calculated. I consider this process less convenient than the one already described.

The writer has used still another method which gives good results, but it is less rapid than those mentioned. After the determination of the hypochlorite and chloride present has been made, the total oxidising power of the original solution, due to the hypochlorite and chlorate contained in it, may be estimated by adding a known quantity to an excess of an acid ferrous solution, containing a known quantity of ferrous sulphate, boiling for a few moments in an atmosphere of carbonic acid, and titrating the unoxidised ferrous salt with potassium permanganate or potassium bichromate. The oxidising power of the original solution can be calculated from the

ferrous iron oxidised by it; and as the hypochlorite present is known, the chlorate present can be calculated.

Absorption of Chlorine.

In testing the efficiency of electrolytic chlorine generators it is most convenient to absorb the chlorine produced in sodium hydrate solution. The amount of chlorine already present in the alkaline solution should be determined by a preliminary analysis. The alkaline solution which absorbs the chlorine will contain it mainly as hypochlorite, but also as chloride and chlorate. A known fraction of the absorbing liquid is taken, made up to 1000 c.c., and of this 50 c.c. are measured and 20 c.c. of sulphurous acid solution and 5 c.c. of nitric acid added, the sulphurous acid removed by boiling, and the total chlorine is then easily found by the method described for the estimation of the total chlorine in the electrolysed solution, and from this the chlorine originally in the solution must be subtracted.

I see no reason why the methods given above may not be applicable to the analysis of bleaching powder in cases where the estimation of total chlorine and chlorate is desirable.—*Technology Quarterly*, iv., No. 4.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolitan Water Act, 1871.

London, August 12th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the total 182 samples examined during the month, one sample had to be noted as "slightly," and six samples as "very slightly" turbid, consequent, doubtless, on the occurrence, occasionally, of violent rainfall. To the same cause also is doubtless attributable a somewhat lessened degree of freedom from colour-tint in the supply generally, the measurements of the colorimeter being appreciably affected by otherwise scarcely noticeable interferences with the transparency and brightness of the water.

Despite these circumstances, however, the general condition of the month's supply was entirely satisfactory, and in respect to the smallness of the proportion of organic matter present, as estimated by the combustion process, was even exceptionally so. The proportion of organic carbon present in different samples varied, however, within a wider range than usual. Thus, among the Thames-derived samples, the proportion ranged from a minimum of 0.040 part to a maximum of 0.152 part; while the proportion in the previous month's samples ranged only from

a minimum of 0.072 part to a maximum of 0.134 part in 100,000 parts of the water.

The mean proportion of organic carbon present in the Thames-derived supplies was found to be only 0.095 part, as against a mean for the month of June of 0.107 part, and for the previous three months, including June, of 0.117 part in 100,000 parts of the water. The mean proportion of organic carbon in the Thames-derived water furnished by the Chelsea Company was, moreover, quite exceptionally low, amounting only to 0.072 part, that of the New River Company's supply being 0.067 part in 100,000 parts of the water.

During the past month we have made an additional series of daily examinations of the unfiltered water of the Thames at Molesey. The proportion of organic carbon was found to range from 0.165 part to 0.195 part, with a mean of 0.182 part in 100,000 parts of the unfiltered water, as against the above mentioned mean of 0.095 in the filtered water distributed. The ratio of organic carbon to organic nitrogen in the unfiltered water was found to be substantially identical with that in the filtered water, being in the former case as 1:0.311 and in the latter case as 1:0.326.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

THE SPECIFIC HEAT OF ATOMS, AND THEIR MECHANICAL CONSTITUTION.

By G. HINRICHS.

In my former paper I have shown that there is between the simple radicle (chemical element) and the complex radicle a mechanical contrast which obliges us to renounce the very general idea of considering the elements as radicles not yet decomposed.

The demonstration given of this principle is novel, but the fundamental principle has been laid before the Academy itself in the memorable discussion on the nature of the elements of chemistry in the Session of December 8th, 1873, by M. Berthelot, who said (*Comptes Rendus*, lxxvii., p. 1352, 1873):—

"In fact, the simple bodies, as we know them, possess certain positive characters which do not belong to the compound bodies, such as the relations existing between the specific heat of a body, its gaseous density, and its atomic weight; relations independent of its temperature."

This declaration of fact, concerning the rational bases of all scientific study of the unity of matter is defined in the following manner (*Loc. cit.*, p. 1356):—

"Between the compound bodies which we know and their polymers there exists this general relation, that the specific atomic heat of a polymer is approximately a multiple of that of the uncondensed body."

On the contrary, the atomic specific heat remains constant for the various elements whose atomic weights are multiples of each other. The same difficulties exist for the hypothesis of a simple body, the atomic weight of which would be the sum of the atomic weights of two others."

M. Berthelot returns to this general principle of thermo-chemistry in the following Session in these terms (*Loc. cit.*, p. 1401):—

"In sum, the study of specific heats, such as the most recent researches have brought to light, leads to the establishment of a positive character which distinguishes, as it seems to me, the simple bodies of chemistry from the compound bodies: it shows that no known compound body can be reputed of the same order as an actual simple body. The importance of such a character cannot be called in question; it increases in virtue of the mechanical

signification which the theories of the present day ascribe to the notion of specific heats. This is what I have endeavoured to bring forward."

The facts established are beyond all controversy; the general principle announced by M. Berthelot constitutes therefore, of necessity, one of the bases of the great problem of the constitution of matter. Every research into the mechanical constitution of the chemical elements ought to take this principle into consideration, and give its mechanical signification. To set aside this fundamental principle would be to avow non-comprehension of the problem, and to seek to discuss on astronomy whilst ignoring the movement of the earth. This is what has been done recently by some distinguished chemists.

There remains the question of the mechanical signification of this thermo-chemical principle of M. Berthelot. Let us give its elementary demonstration which results from my formulæ published in 1872 ("Beiträge zur Dynamik des Chemischen Moleküls," *Deutsch. Chem. Gesell.*, May 11, 1872), and 1873 (*Comptes Rendus*, lxxvi., p. 1358), and which agree with the general constitution of the atoms of the elements in my "Programme de la Mécanique des Atomes," of 1867:—

"Let m be the mass of an elementary atom (simple radicle), and v its maximum undulatory velocity. In like manner, for an atom composed of n atoms m , let M be the total mass and V the velocity of the centre of gravity. We shall have—

$$(117). \quad M = \Sigma m,$$

$$(118). \quad 2E' = \Sigma m v^2 + M V^2$$

if we call the total energy of the vibrations E' . For more complete formulæ I must refer to *Comptes Rendus* (lxvii., p. 1358, 1873) and to the recent edition of my "Beiträge" of 1872 (G. Fock, Leipzig, pp. 3–6, 1892).

But according to thermodynamics we have—

$$(119). \quad M V^2 = 2k T,$$

T being the absolute temperature, and k a constant. In like manner we have—

$$(120). \quad m v^2 = 2\rho k T,$$

where ρ is another constant.

We have then the expression of all the actual energy except that of rotation—

$$(121). \quad E' = k(1 + \rho n) T.$$

The atomic specific heat, representing the vibrations only, will therefore be—

$$(122). \quad s' = \frac{dE'}{dT} = k(1 + \rho n).$$

This formula shows that the specific heat of the atoms increases almost proportionally to the number, n , of the atoms contained in the compound or complex radicle.

For the chemical elements this atomic heat is, according to experiment, constant and independent of n . Therefore ρ ought to be null; that is to say, that the velocity of vibrations of the constituent atoms, m , ought to be null [see (120)].

The mechanical signification of Berthelot's thermo-chemical principle may, perhaps, therefore be formulated as follows:—

"In chemical compounds the atoms of the elements enter as integrant individualities, retaining a specific vibratory movement; but the atoms of the true chemical elements are solid or liquid bodies, the constituent atoms of which have no individual movements.

In presence of this general result, it is not surprising that the chemical elements have hitherto resisted all the efforts hitherto made for their decomposition. The establishment of the mechanical constitution of the elements has been the supreme object of my studies for thirty-eight years. I hope to be able to publish my final results before a year from the present date; but, in order to succeed, it will be necessary to establish several other laws of the mechanics of atoms. I must therefore resume

the study of the ebullition points as a function of the form of atoms of known composition. Having considered the terminal substitutions, I must study the central substitutions in an early study.—*Comptes Rendus*, cxv., p. 239.

ON A NEW CLASS OF COMPOUNDS, THE NITRO-METALS; AND ON THE PROPERTIES OF NITROGEN PEROXIDE.

By PAUL SABATIER and J. B. SENDERENS.

THE oxidising properties of nitrogen peroxide (hyponitric acid) are more active than those of nitric oxide, previously studied, and the products yielded are generally in a more advanced state of oxidation.

Lower Oxides.

Manganous oxide, MnO , in nitrogen peroxide is oxidised at about 350° , yielding manganese sesquioxide (manganese per cent—found, 69.6; calculated, 69.1.

Titanium sesquioxide is oxidised at 300° , as in air and nitric oxide, yielding white titanic acid, TiO_2 .

Tungstic bixide (brown), TuO_2 , reacts below 300° with incandescence; the product is similar to that formed in air, i.e., yellow tungstic acid, TuO_3 , mixed with a little blue oxide.

Black vanadium oxide, Va_2O_3 , is oxidised at from 300° to 400° and is totally transformed into yellow-brown vanadic acid, Va_2O_5 .

Red cuprous oxide, Cu_2O , which is not affected by nitric oxide, is converted by nitrogen peroxide at 300° into black cupric oxide.

Metals.

Aluminium filings are not appreciably oxidised even at 500° .

Magnesium filings react only at dull redness, when they display a very energetic combustion.

Zinc is very regularly oxidised about 300° .

Lead is slowly oxidised above 200° , and yields white basic nitrate.

The metals obtained on reducing the oxides by hydrogen present a quite special interest.

Reduced nickel reacts with incandescence at 250° , yielding protoxide, which is merely greyish.

Reduced iron is oxidised with incandescence about 350° , yielding ferric oxide.

Reduced cobalt burns briskly at the common temperature in nitrogen peroxide, and forms black oxide, Co_3O_4 .

Reduced copper is converted at 250° into black oxide, CuO , but in the cold it reacts upon nitrogen peroxide, giving a special compound which we shall describe in detail.

II.—Nitro-metals.

Pure dry nitrogen peroxide can fix itself in the cold upon certain metals, forming special compounds which we propose to call "nitro-metals."

Reduced copper absorbs in the cold the vapours of nitrogen peroxide with a disengagement of heat perceptible to the touch. When this action has ceased, there remains a maroon compound, the composition of which is represented by the formula Cu_2NO_2 . The increase of the weight of the copper during fixation yields an indirect method of analysis, which has been checked by the ulterior analysis of the product.

The compound reacts violently with water, yielding nitric oxide, which is entirely absorbable by ferrous sulphate, yielding a green liquid which contains copper nitrate mixed with a little nitrite. There remains a residue of copper almost absolutely pure. The proportion of copper dissolved varies, according to the duration of the reaction, from 11.1 to 13.4 per cent.

If heated in pure dry nitrogen, the substance disengages

nitrogen peroxide in abundance, and there remains copper mixed with a certain proportion of oxide; one-third of the oxygen is thus retained.

If it is heated in a sealed tube the same reaction takes place, and we may liquefy nitrogen peroxide in a refrigerated portion of the tube. A re-absorption takes place anew in part by the metal not oxidised.

The preparation of nitro-copper requires that the nitrogen peroxide must be free from traces of nitric acid which it may contain, and which is derived especially from the energetic action upon the caoutchouc connections. This nitric acid reacts upon the compound, which it gradually destroys with effervescence, forming the green nitrate. We may succeed in completely eliminating it by placing in front of the boats, in the reaction tube itself, a column of litharge followed by a column of phosphoric anhydride. The litharge absorbs the nitric acid, and the phosphoric anhydride takes up the water which may possibly have been formed by the reaction of the litharge.

Reduced cobalt, as it has been mentioned above, burns in the cold in the vapour of nitrogen peroxide. This ignition may be avoided by suitably diluting the vapours of peroxide with a current of pure dry nitrogen. We then observe a reaction absolutely similar to that given by copper; we find a disengagement of heat, which continues as long as the fixation takes place. When it has ceased nitro-cobalt remains as a black compound, the composition of which corresponds exactly to the formula CO_2NO_2 .

Its reaction with water is extremely lively, but less gas is given off than in case of nitro-copper. We obtain a rose coloured solution of cobalt nitrates containing very little nitrite. At the same time there occurs a precipitation of insoluble bluish green basic nitrite, which is found mixed with metallic cobalt.

Nitro-cobalt, if slightly heated in a current of nitrogen, evolves at first a little nitrous vapour, then almost immediately it deflagrates with an extraordinary lustre, leaving a residue of metallic chloride peculiarly oxidised. If it is mixed with a combustible matter, there occurs an explosive deflagration.

We are pursuing the chemical study of these compounds, and at the same time the preparation of new nitro-metals.—*Comptes Rendus*, cxv., p. 236.

THE SOLUBILITY OF THE PHOSPHORIC ACID OF BONE-MEAL.

By H. OTTO.

THE consumption of bone-meal in the West of Germany has declined so much during the last two years that producers find it difficult to dispose of a good product even at low prices. The cheapness of superphosphates, and especially the extraordinary demand for basic slag meal, are the principal causes.

Probably no manurial substance has given rise to so many publications and theoretical researches as basic slag. In P. Wagner's memoirs on this subject the phosphoric acid of basic slag is almost without exception represented as superior to the phosphoric acid of other manures. It is in the first place remarkable that in Wagner's comparative manurial experiments the efficacy of bone-meal takes so low a relative position. In these experiments it seems to have resulted that the phosphoric acid of bone-meal scarcely occasioned an increase of the crop, and that its efficacy was always less than that of the phosphoric acid of basic slag.

Quite opposite views are put forward in the publications of Prof. Marek, of Königsburg, and Prof. Holdeffleiss, of Breslau. The latter, in his treatise on "Das Knochenmehl, seine Beurtheilung und Verwendung" (Bone-meal, its Valuation and Use), says (p. 168), referring to the experiments of Marek: "According to these decidedly

trustworthy results bone-meal has a considerable manurial value, so that it may be included among the most certain and efficient manures. This conclusion is the more trustworthy as it agrees with the practical experience of many decennia and is fully confirmed daily.

These contradictions can scarcely be accidental, and I can only assume that the bone-meal used in Wagner's experiments was not a good product. The chief part of the bone-meal at present met with in commerce is produced from bones which have been freed from fat by means of benzene. The meals are either simply ground bones, or mixtures of bone-meals freed from glue, and so called "stamp-meal," obtained in the manufacture of granulated bones. Of the mixtures of horn-meal, blood-meal, crude phosphates, and a little bone-meal, which unfortunately are also met with in trade, I am not about to speak. These occur now less and less frequently since several experimental stations have declared an energetic war against them.

The bone-meal obtained from bones deprived of fat contains always from $4\frac{1}{2}$ to 5 per cent nitrogen, and 21 to 23 per cent phosphoric acid (P_2O_5), rarely more than 2 per cent of fat, generally less; all bone-meals containing less than 4 per cent N and 20 per cent P_2O_5 are not pure degelatinised meals, or the entire substance of the bone has not been used in their manufacture.

It is remarkable that such a bone-meal which, according to Heyden, Holdeffleiss, Marek, &c., is an excellent manure, should prove inert according to Wagner.

When the basic slag in the state of meal was especially recommended to farmers as an especially effective phosphoric manure, it was sought to prove the solubility of the phosphoric acid by means of Wagner's citrate solution. In fact, the phosphoric acid of basic slag, if ground sufficiently fine, is to a great degree soluble in this citrate.

In the conviction that a bone-meal almost deprived of fat must give up its phosphoric acid to a slightly acid solution of ammonium citrate, I examined various samples of bone-meal exactly according to Wagner's citrate method as laid down on December 19, 1885, and found that according as the meal had been more or less finely ground from 8.05 to 9.15 per cent of the P_2O_5 was rendered soluble, or from 38.28 to 41.20 per cent of the total weight of the meal.

From these results it is clear that the phosphoric acid of bone-meal freed from fat, but not from gelatin, is very readily soluble. If we consider further that on account of the large percentage of gelatin the solubility in the soil will be increased by the products of decomposition formed during decay we may assume with certainty that such bone-meals must possess a considerable manurial value.—*Chemiker Zeitung*, August 6, 1892.

THE COMPOSITION OF ANCIENT MORTAR.

MR. JOHN HUGHES, F.C.S., has contributed to the *Builder* an article on this subject, from which we quote the subjoined analyses.

The author deduces the following practical conclusions from these analyses:—

1. That the actual amount of lime present in a mortar may vary very considerably, but that within certain limits the quality of the lime is of great importance as the quantity,—indeed, a smaller quantity of well-prepared good lime is much more effectual than a larger quantity of a badly prepared or naturally inferior lime.

2. That the proportions of sand may also vary considerably, even in really good mortar, and that while it is always desirable that it should be rough, irregular in size, and with sharp edges, rather than be smooth and round, still that, on the whole, the quality of the sand is not of so much importance as the quality of the lime.

3. That the presence of oxide of iron and alumina in a

Analyses of Ancient Mortar.

	No. 1. Tintern Abbey.	No. 2. Caerphilly Castle.	No. 3. Raglan Castle.	No. 4. Giant's Tank, Ceylon.	No. 5. Rochester Castle.	No. 6. Glastonbury Abbey.	No. 7. Glendalough Church, Ireland.	No. 8. Corfe Castle.
Probable date of erection, about A.D.	1269.	1200.	1200.	1250.	1088.	1246.	Not known.	1000.
Water (lost at 212° F.) . . .	1'72	2'60	1'36	1'18	0'36	4'96	0'55	2'42
Combined water	3'98	7'73	4'06	2'66	1'48	4'94	2'92	4'02
Lime**	18'84	13'49	30'68	16'24	28'67	36'46	10'59	31'05
Magnesia	0'32	1'87	0'25	0'36	0'18	0'45	0'43	0'28
Potash	0'02	0'22	0'15	0'30	0'16	0'33	0'25	0'20
Soda	0'27	0'29	0'45	0'17	0'24	1'18	0'13	0'15
Oxide of iron	1'99	3'61	1'35	2'20	0'40	3'60	1'58	0'95
Alumina	1'36	1'34	0'80	2'65	0'30	1'45	0'71	0'15
Sulphuric acid	1'37	0'34	0'86	0'58	0'29	0'89	0'32	0'26
Carbonic acid*	12'13	9'53	21'01	11'11	20'60	25'06	6'40	22'86
Chlorine	0'13	0'01	0'15	trace	0'10	0'88	0'14	0'65
Gelatinous silica, soluble in alkali	6'20	9'85	4'10	7'10	1'60	6'10	3'90	7'50
Insoluble matters (sand) . .	51'67	49'12	34'78	55'45	45'62	13'70	72'08	29'51
	100'00	100'00	100'00	100'00	100'00	100'00	100'00	100'00
*Equal to carbonate of lime . .	27'56	21'66	47'75	25'25	46'81	56'95	14'54	51'95
{ Lime present as carbonate . .	15'43	12'13	26'74	14'14	26'21	31'89	8'14	29'09
{ Lime present as caustic . .	0'28	0'56	0'84	0'56	0'56	0'56	0'84	0'28
** { Lime present as sulphate . .	0'95	0'23	0'60	0'40	0'20	0'62	0'22	0'18
{ Lime present as silicate and otherwise combined . .	2'18	0'57	2'50	1'14	1'70	3'39	1'39	1'50
	18'84	13'49	30'68	16'24	28'67	36'46	10'59	31'05

form readily combined with silica is not to be objected to in good building lime; indeed, that the purest limestones are by no means the best for making superior lime for building purposes.

4. That the higher the proportion of amorphous or gelatinous silica soluble in alkali the better the quality of the mortar, and as this kind of silica is associated originally with the lime, rather than with the sand, it becomes of the greatest importance that the character and composition of the lime intended to be used should be fully inquired into, and the best possible quality in the neighbourhood always selected by the architect and used by the builder.

CORRESPONDENCE.

WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—It is with extreme regret that I observe a recommencement of the "water analysis" controversy in your columns.

To my mind it is not only useless but derogatory to English science to wage a bitter wordy war concerning the merits of two rival processes, neither of which does more than give an approximation to the quantities of certain substances, the presence of which is only circumstantial evidence of the character of a water.

Instead of wasting our time in acrimonious discussion, cannot we English chemists combine our forces and search for other processes giving more definite information? We have many reagents for separating nitrogenous organic substances, certain of which, I take for granted, furnish the strongest evidence of pollution. Among these reagents I may enumerate tannin, salts of mercury, bismuth, cadmium, &c., phosphotungstic acid, saturated solutions of ammonium sulphate, sodium chloride, &c., and others will readily occur to the minds of your readers.

Would not our position as scientific men be stronger and more dignified if we made attempts to gain informa-

tion on the above lines? As the work will be long and tedious we should combine, and even invite the co-operation of our foreign colleagues; thus we shall certainly spend our energies with more profit than by mere argument.—I am, &c.,

H. DROOP RICHMOND.

50, Clanricarde Gardens,
Bayswater,
August 29, 1892.

WATER ANALYSIS.

To the Editor of the Chemical News.

SIR,—In a letter which appears in your last number Mr. J. Alfred Wanklyn states that I have quite recently been made Chemical Adviser to the Local Government Board, that I am forcing my process of water analysis upon reluctant chemists, that the correction for experimental errors in my laboratory is "0.32 m.grm. of carbon and 0.045 m.grm. of nitrogen per litre of water," and that in certain experiments with sulphate of quinine "the experimental carbon and nitrogen agreed exactly with the calculated quantities, but the calculated quantities were wrongly calculated." I rarely notice Mr. Wanklyn's wild and erroneous utterances, but in this case must ask you to kindly allow me space to say that these statements are, one and all, absolutely false.—I am, &c.,

E. FRANKLAND.

Leamington, August 31, 1892.

SOLAR RADIATION.

To the Editor of the Chemical News.

SIR,—The question of what becomes of the superfluous heat radiated from the sun and apparently lost in space, meeting with no solid body to absorb it, is one that has long exercised the minds of thinking men. Such waste seems little in keeping with the law of the "conservation of energy which pervades all Nature."

Some years ago a solution of the difficulty was propounded by the late Sir W. Siemens, which, though ex-

tremely ingenious, did not strike one as very probable, though in the absence of any other, and coming as it did from so great an authority, was admitted by many as possible.

I do not know if it has ever been conjectured that the radiations are probably absorbed by the highly attenuated matter with which many suppose that the entire regions of space are filled. But may not such be the case, and is there any reason to the contrary? Gases and vapours are diathermanous in various degrees according to their nature, and according to the activity of the heat radiations which are transmitted through them; but they all surely must exert some absorbent effect, though the rise in temperature may be inappreciably small; if so, in infinite space all the heat would at length be taken up. If, then, the radiations are so absorbed, they go to increase the volume, though ever so imperceptibly, of the ultra-gaseous matter, and are utilised in increasing the trajectory of the vibrations of each of its material particles, so that the heat would not be wasted, but would be stored up in the universe perhaps to play its part in the production of fresh worlds or the evolution of new elements, and perhaps to be diffused again into space and to seek fresh matter with which to become associated. It is even conceivable that if the temperature of the sun and the other stars is maintained, as some persons suppose, by the impact of meteor swarms, the heat which has been absorbed by the ultra-gaseous matter contained in the limitless regions of space may by these means be restored to its original source in lapse of time.—I am, &c.,

F. MAXWELL LYTE.

London, Aug. 29, 1892.

ESTIMATION OF CAOUTCHOUC.

To the Editor of the Chemical News.

SIR,—I am not aware of any method which enables us to estimate caoutchouc as a principle. It is usual in analyses to state the quantity by difference, but of course any substance present which disappears on combustion, &c., will make an article appear richer in caoutchouc than it actually is. Lead oxides are reduced by carbon and volatilised. Carbon and carbonic acid also disappear.

Presuming that the mat supplied by M. Guibal was vulcanised, how is 40 per cent caoutchouc estimated in presence of 15 per cent "vulcanised clippings"? In an uncured mixture it is possible by solvents to separate cured from uncured rubber if present.

Will two parts sulphur vulcanise forty parts caoutchouc in the presence of thirty-five parts litharge? It is well known that the sulphur used varies with the different descriptions of caoutchouc met with in commerce, and also with the same rubber according to its intended use. Litharge will take up more or less sulphur, leaving a diminished quantity for vulcanising. Sulphurous acid gas vulcanises, but it is doubtful whether the quantity formed would compensate for the sulphur lost as lead sulphide.

Again, why is lead estimated as litharge in a vulcanised mixture? or is lime present only as chalk? How can 2 per cent sulphur be fixed on when the mixture contains 15 per cent "vulcanised clippings." It is no less interesting to know how the 15 per cent was determined?

I may venture to say that 35 per cent litharge was a needless addition, and that it must have added to the expense of the mat in increasing its specific gravity, which is of fundamental importance, but which unfortunately is not stated.

The statements of M. Payen with respect to gutta-percha resins are unreliable. I have rarely met with a sample of raw gutta-percha containing less than from 45 to 55 per cent resins. A portion of this can be removed.

If a sample be boiled for some hours in a flask on a water-bath with an inverted condenser, and the operation

repeated with fresh spirit until it ceases to give up anything more, being carefully laminated before each boiling, it will require at least a week's boiling. The solvent may be either a mixture of alcohol and ether, which acts quicker, or a mixture of equal parts absolute alcohol and rectified spirit of wine.

In addition to the two resins named by Payen, alban (white resin) and flavan (yellow resin), a third resin is present, which is probably an oxidised gutta-percha. Neither of these resins are saponifiable in an aqueous solution of soda.

Alban and flavan may be partially separated from each other, as alban is soluble in boiling alcohol and deposits on cooling. Flavan remains in solution, and by concentrating a further deposit of alban takes place. Alban and flavan are soluble in alcoholic potash solution: the third resin is not soluble in this liquid, and so admits of separation.

The quantity of resins present in gutta-percha will vary with the methods of collecting; for instance, 80 to 90 per cent, consisting principally of alban, may be found in the gutta-percha recovered from the bark of these trees yielding good gutta-percha when the lactescent juice is drawn from the wood.

The resins are probably modifications of gutta-percha; by destructive distillation they yield products which are obtained when this substance is similarly treated.—I am, &c.,

ELECTRON.

Detection of Resorcin.—L. Reuter (*Pharm. Zeitung und Chemiker Zeitung*) dissolves 0.1 grm. of substance in 50 grms. potassa lye, heats a few c.c. of this colourless solution in a test-glass at the temperature of the water-bath, and adds a few drops of chloroform or bromoform, or a minute crystal of chloral hydrate or bromal hydrate. The liquid soon takes an intense red colour. This reaction, which is extremely sensitive, was indicated by Guareschi as far back as 1872.

Recognition of Furfural.—E. Nickel (*Chemiker Zeitung*).—The substance in question is submitted to dry distillation in a clean test-glass free from dust (Schiff) or cautiously heated with a small excess of concentrated sulphuric acid (Von Udransky). In either case there are formed vapours of furfural, which give a red colour to paper charged with salts of aniline or xylydine. If it is desired to detect furfural in solution, the reagents used are certain phenols (α -naphthol), phloroglucine, or biliary acids (cholic acid).

Meeting of the Association of Bavarian Chemists at Regensburg, August 2nd and 3rd, 1892.—Herr Stockmeier (Nuernberg) discussed the acidity of paper and the determination of mechanical wood-pulp. After describing the various methods proposed, he explained the injurious action which acidity in paper may occasion in many of its uses. S. Metzger treated on the decision upon vinegar. An essential condition in the preservation of vinegar is the use of clean, tightly closing casks. Still, in spite of all care, "vinegar-eels" (*Anguillula exophila*) make their appearance, and collect at the bottom of the casks, whence they are dislodged on agitation—as it is frequently practised on drawing samples—and become distributed through the entire cask. The assumption, however, that the origin of the eels is connected with impurities, or with an insufficient strength of the vinegar, is erroneous. Vinegar-eels may be found even in a 12 per cent "distilled vinegar." According to the researches of Pasteur we possess no other permissible process for preventing the development of vinegar-eels than Pasteurising. In the ensuing discussion Borgmann (Wiesbaden) pointed out that, according to Pasteur, the eels require air for their existence. If this condition is wanting they speedily perish. To a question put by Janke (Bremen) whether these eels occur in vinegar prepared from distilled vinegar, the author replied that this is not the case.—*Chemiker Zeitung*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 4, July 25, 1892.

Certain New Observations on the Use of the Calorimetric Bomb.—M. Berthelot.—The author distinguishes three cases which require different conditions, *i.e.*, fixed compounds, solid or liquid, combustible gases, and volatile combustible compounds.

Study of Boron Trisulphide.—Henri Moissan.—This paper will be inserted in full.

Researches on the Chemical Constitution of the Peptones.—P. Schutzenberger.—The author's first results refer to the fibrine of horses' blood and its transformation into peptone under the influence of the pepsine of commerce in presence of hydrochloric acid. Peptonised fibrine, taken in its totality, differs from the initial fibrine only by the elements of water. It is not a homogeneous product, but may be split up by various methods into distinct products, the examination of which will form the subject of a future memoir.

Formation-Heat of Permolybdic Acid and the Permolybdates.—E. Péchard.—Permolybdic acid is formed with the absorption of heat. Its formation necessitates the intervention of extraneous energy, and in its production this energy is supplied by the heat liberated in the decomposition of oxygenated water.

Crystalline Mercury Phosphide.—M. Granger.—At ordinary temperatures, whether under normal pressure or in sealed tubes, phosphorus has no action upon mercury. The author has obtained the compound Hg_3P_2 by causing phosphorus iodide and mercury to react in sealed tubes at from 275° to 300° . The compound is permanent in the cold, but in heat it is decomposed into its elements. It ignites if heated in contact with air, and if mixed with potassium chlorate it detonates under the hammer. Nitric and hydrochloric acid have no action upon it, but it dissolves easily in *aqua regia*.

Mineralising Action of Ammonium Sulphate.—T. Klobb.—On treating copper salts with ammonium sulphate, the author has obtained in succession according to the temperature a double copper ammonium sulphate; (2) the sulphate SO_4Cu ; (3) basic sulphate $2CuO, SO_3$, and lastly cupric oxide. The double sulphate forms transparent light green prisms, about 1 m.m. in length, and of specific gravity 2.85. The author is further studying the action of ammonium sulphate upon the salts of chromium and uranium.

Micrographic Analysis of Alloys.—Georges Guillemin.—The researches of MM. Osmond and Werth undertaken to determine the structure of cast steel have led the author to make similar investigations of the industrial alloys of metals other than iron. He attacks a polished surface of such alloys either with cold dilute nitric acid or with sulphuric acid (1:10) under the influence of a weak electric current, and examines the surfaces with the microscope. The images obtained, which are afterwards photographed, are always invariably the same for any given alloy. The microscopic examination of surfaces of brass or bronze show accurately if aluminium or phosphorus has been added. If a brass contains aluminium the grooves or furrows observed take constantly the form of veins of marble or conglomerates. This holds good even if the aluminium is in such minute quantities that its presence is not readily detected by the methods of analytical chemistry. In fine, micrographic analysis renders it possible to determine rapidly and summarily the nature of a bronze or other alloy by the simple inspection of a surface polished and corroded, and

to recognise if the alloy has been simply cast or if it has been only stamped, laminated, or drawn.

Homopyrocatechine, and on its Two Nitro-derivatives.—H. Cousin.—The composition of the two compounds is respectively represented by the formula $C_7H_7NO_4$. The second compound is an isomer of the former. It melts at about 180° , whilst the former melts at 79° to 80° .

New Class of Compounds, the Nitro-Metals, and on the Properties of Nitrogen Peroxide.—Paul Sabatier and J. B. Senderens.—(See p.).

The Specific Heat of Atoms and their Mechanical Constitution.—G. Hinrichs.—(See p.).

Monopropylurea and Non-Symmetric Dipropylurea.—F. Chancel.—The former compound is neutral to litmus; it melts at 107° when quite dry, and it is very soluble in water and alcohol. The nitrate and oxalate are very soluble in water, out of which they crystallise badly. They are also very soluble in alcohol, on the evaporation of which the nitrate yields fine needles. The non-symmetric dipropylurea is also neutral to litmus; it melts at 57° and is very soluble in water and alcohol, sparingly soluble in saturated solutions of potassium sulphate. The neutral oxalate is sparingly soluble in water, from which it crystallises in fine needles; it has an acid reaction with litmus. The nitrate is a non-crystallisable syrup.

The Composition of Fossil Bones and the Variation of their Proportion of Fluorine in the different Geological Epochs.—Ad. Carnot.—The author finds in the specimens which he has examined a progressive increase of fluorine with the age of the specimen. The proportion of fluorine is in many fossil bones 10 or 15 times as great as in modern bones, referred to the same weight of ash. He suggests that a determination of fluorine may assist in fixing the age of bones.

Distribution and State of Iron in Barley.—P. Petit.—Almost all the iron is found in barley in the state of nucleine.

The Comparative Toxicity of the Alkaline and Earthy Alkaline Metals.—Paul Binet.—The author's experiments with lithium, sodium, potassium, magnesium, calcium, strontium, and barium, in the state of chlorides, have been made by the subcutaneous method upon warm blooded animals and upon frogs. The general results are:—(1) The most general effect exerted by metallic salts upon the organism is the loss of excitability of the nervous system, central and peripheric, and then an alteration of muscular contractility. (2) This ultimate stage is preceded by disturbances of respiration and of the heart, which may occasion a rapid death before any other symptom. In warm-blooded animals we may, even on subcutaneous injection, observe gastro-intestinal troubles: vomiting, diarrhoea, especially with barium and lithium. (3) In addition to their general action the metals are distinguished from each other by their particular characters, which render it possible to establish a relation between the nature of the physiological action exerted by the metal and the place which it occupies in the chemical classification. (4) The natural group, lithium, sodium, potassium, is characterised by the stoppage of the heart in diastole, weak motor inertia without contractions; the group calcium, strontium, barium, is characterised by the stoppage of the heart in systole, and the tendency to contractions especially in the case of barium. (5) Calcium is further distinguished by the special action which it exerts upon the nerve centres, a state of torpor with retention of reflex excitability and sensitiveness. (6) Magnesium approximates to the first group by the stoppage of the heart in diastole, but it deviates from the other metals by the early paralysis of the peripheric nervous system. It is a motor-paralyser like curare, but it is distinguished from the latter by interfering less readily with respiration. (7) According

to the intensity of their poisonous action, studied upon the frog, these metals may be classified in the following decreasing order: lithium, potassium, barium, very poisonous; calcium and magnesium, much less poisonous; strontium, slightly poisonous; sodium, scarcely poisonous at all. Among the mammalia the order is rather different; for them barium is by far the most poisonous. (8) Contrary to the law proposed by Rabuteau, there is no constant relation between the toxicity of a metal and its atomic weight; this relation cannot even be found among the elements of the same group. (9) The author refers to the special tolerance of the organism for sodium as being probably due to ancient adaption to a saline medium.

Colourless Globuline possessing a Respiratory Function.—Dr. A. B. Griffiths.—This globuline has been extracted from the blood of *Patella vulgata*. Its molecule contains no metal, and it possesses the same properties of oxygenation and deoxygenation as do hæmoglobine and hæmocyanine. The author names this compound achroglobine, and assigns to it the formula $C_{523}H_{761}N_{196}SO_{140}$.

Vol. cxv., No. 5, August 1, 1892.

On Boron Pentasulphide.—Henri Moissan.—Boron pentasulphide possesses properties which distinguish it clearly from the trisulphide. Its melting-point is 390° , whilst the trisulphide begins to melt at 310° . Its manner of fusion differs also from that of the trisulphide; it does not pass through a pasty condition, but becomes immediately liquid as soon as the temperature of 390° is reached. In contact with water it is resolved at once into boric acid, sulphuretted hydrogen which escapes, and sulphur which is deposited, whilst the pure trisulphide never gives a deposit of sulphur. Whilst the trisulphide is not attacked by mercury and silver, even at a dull red heat, this new compound is easily attacked by these metals, forming boron trisulphide and a metallic sulphide. The action of mercury is very characteristic. The vapour of mercury attacks this compound with incandescence; mercury sulphide distils, and there remains melted boron trisulphide.

Constitution of Pyrogallol.—M. de Forcrand.—A thermo-chemical paper, which does not admit of useful abstraction.

On Cascarine.—M. Leprince.—Cascarine is a proximate principle obtained from the bark of *Rhamnus fruticosa*, known by the Spaniards as *Cascara sagrada*. It forms prismatic needles of an orange yellow. It is tasteless and inodorous, soluble in alkaline solutions, with a dark purple-red colour. It is insoluble in water, soluble in pure alcohol and in ether-alcohol, less soluble in chloroform. If perfectly dried its composition is $C_{12}H_{10}O_5$. The author raises the question whether cascarine is identical with rhamnatin, or if they are merely isomeric.

Properties of the Vapours of Formal or Formic Aldehyd.—F. Berlioz and A. Trillat.—These vapours diffuse themselves rapidly in the animal tissues, which they render incapable of putrefaction. Even in slight proportions they oppose the development of bacteria and other organisms. They sterilise in a few minutes substances impregnated with the bacillus of Eberth and that of splenic fever. The vapours are not poisonous unless inhaled for some minutes and in large quantities.

each from Belgium, Sweden, and North America; one each from Austria, Switzerland, Holland, France, Spain, England, Russia, Roumania, and Java. There are three assistants in the tuitional laboratory, three in the experimental station, and sixteen in the various departments of the laboratory of research. The staff includes, in addition to the Principal, Professors H. Fresenius and Borgmann, Drs. W. Fresenius, E. Hintz, Frank, and the architect Brahm. The next term begins on October 17th. In addition to scientific work (pure) there have been conducted, during the summer, numerous investigations in the interest of commerce, the arts, mining, agriculture, public health, and justice.

Commercial Potassium Cyanide.—According to the *Chemiker Zeitung* (1892, No. 64), Dr. Kayser, of Nurnberg, read a paper on this subject before the eleventh meeting of the "Free Association of Bavarian Representatives of Applied Chemistry." The kinds of potassium cyanide at present generally met with in commerce consist largely of a mixture of potassium cyanide and sodium cyanide. This circumstance must be remembered in examinations of potassium cyanide. If we simply determine the quantity of cyanogen, and calculate the result as potassium cyanide, a commercial sample containing 15 per cent impurities may easily be reported as potassium cyanide of 100 per cent. The presence of considerable quantities of sodium cyanide is further not indifferent in many technical applications. Thus, in preparing galvanic gold-baths from gold as anode in a solution of potassium cyanide and sodium cyanide by means of the galvanic current, there is obtained not the readily soluble potassium aurocyanide, but the very sparingly soluble sodium aurocyanide. The latter on its origin is at once deposited on the anode, and we do not succeed in obtaining a useful gold-bath. According to the view of the speaker it is possible that the advice of Wagner has been followed in the manufacture of the ferrocyanide. Wagner, namely, from technical reasons, recommended the use of a mixture of potash and soda, and that the resulting mixture of potassium and sodium cyanides should be sold under the name of "cyanogen salt." Prof. Fresenius confirmed the presence of sodium ferrocyanide in the potassium ferrocyanide of commerce.

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MISCELLANEOUS.

The Wiesbaden Laboratory.—According to the *Chemiker Zeitung* the laboratory of Prof. Dr. R. Fresenius has, during the summer term, been attended by fifty-eight students. Of these forty-three are from Germany; two

THE CHEMICAL NEWS.

VOL. LXVI., No. 1711.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

It has often been asked why so few of the best minds in this country turn their attention to scientific research? The answer commonly and bluntly given is because research does not pay. The emoluments which fall to the lot of the greatest discoverer are trifling compared with those which he might have realised with less labour in various other departments of activity. Had he given his mind to theology he might have become a prelate. Law might have showered upon him not merely heavy fees and refreshers, but might have earned him a title. But Science had nothing to offer but the gratification of the love of truth. Sir Isaac Newton, we are told, had been living in these days could scarcely have earned salt to his food. Darwin, so far from being enriched by his discoveries, could not have carried out his investigations except he had been born to an ample fortune. He received no pay for serving on the memorable voyage of the *Beagle*, but had, in vulgar phrase, to find himself. Nor was the discoverer compensated by honours or social position for the lack of material rewards. We have, indeed, had amongst the aristocracy men of genius, such as Robert Boyle and Henry Cavendish. The names of Lords Rayleigh and Walsingham are honourably known. But these *savants* inherited their peerages, and would have held the very same rank had they been the most utter blockheads. In short, until within the last few years the highest rank which a *savant*, as such, could hope to reach was that of baronet.

As a matter of course, young men were warned by their friends not to enter upon so barren a career. We are, indeed, told that men of Science should be above all such considerations. Unfortunately men of Science have the same wants, the same aspirations as other mortals, and when they find that those wishes cannot be gratified in the service of Science they are very apt to look elsewhere.

But now a new day seems to be dawning. We do not know—and we care little—to whose initiative the change is owing, whether to Her Majesty personally, to the late administration, or to their successors. All we hope is that the change may be permanent, and that an honourable ambition may find its reward in the realms of Science as readily as in those of law or finance.

No one, we trust, will be perverse enough to hint that we advise young men to study physics or chemistry in view to a possible peerage. Such a reward will scarcely fall to the lot of one in ten thousand. But the honours conferred upon Lord Kelvin and Lord St. Andrews,—honours which can be understood even by the most stolid Philistine,—will irradiate and encourage even the humblest of their colleagues.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of Two pounds to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of one pound, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

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If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within

three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held July 16, 1893.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held October 15, 1893.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so named, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within

the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, and with especial reference to his Dissertation or Thesis.

Candidates for the Degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

In October, 1892, modifications of the Regulations for the Degree of D.Sc. will come into operation, particulars of which can be obtained of the Registrar.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

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Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £10 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass at the same time in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN. TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, D.Sc., M.D., F.R.S., V.P.C.S.

Assistant Lecturer.—Emil A. Werner, F.C.S., F.I.C.
Demonstrator.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; advanced, second year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry.—J. M. Thomson, F.C.S.
Demonstrator of Practical Chemistry.—G. S. Johnson, F.C.S.

Assistant Demonstrator.—Herbert Jackson, F.C.S.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—Daily attendance: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three months, £6 6s.; Six months, £11 11s.; Nine months, £15 15s.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1892-93, are Tuesday, October 4, Wednesday, January 11, and Wednesday, April 19.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

PHOTOGRAPHY.

Lecturer.—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professors.—R. T. Plimpton, Ph.D., and J. N. Collie, Ph.D.

Assistants.—H. W. Picton, B.Sc., and P. B. Williams.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Monday, October 3rd, until Wednesday, December 21st;

Second Term, from Tuesday, January 10th, 1893, till Saturday, March 25th;

Third Term, for Lectures, from Tuesday, April 18th, till Friday, June 30th. Class Examinations begin on Monday, June 19th.

Junior Courses.

First Term: Tuesday, Thursday, and Saturday, at 10, commencing October 7, 1892. Third Term: Tuesday and Thursday at 10, Friday at 4, beginning April 14th, 1893. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms: Inorganic.—The Class meets four times a week: Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 6th.

Fee:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday, at 9, and Saturday, at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11, commencing October 7th.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1892-93; also the Clothworker's Scholarship of £30.

Chemical Technology.

Lecturer, Watson Smith, F.I.C., F.C.S.

Courses of Lectures will be given on the following subjects:—Manufacture of Sulphuric Acid, Alkali, &c. Fuel and Gas Manufacture. Chemical Technology of Building Materials. Methods for the Technical Chemical Analysis of Raw and Manufactured Products. Coal-tar Products and Colours. Applications of Chemistry to Engineering. Methods of Technical Chemical Analysis.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.

Assistant Professor.—W. P. Wynne, B.Sc., A.R.C.S.

Demonstrators.—H. Chapman Jones and A. E. Tutton.

Assistants.—G. S. Newth, J. W. Rodger, and W. Tate.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 5th of October and ends about the middle

of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany .. .	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	4	13
Mining	4	
Agriculture	4	
Astronomical Physics .. .	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Geometrical Drawing £3 per session. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science Directory may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-first Session will commence on Wednesday, October 5th, 1892. Entries not previously arranged with the Dean or Secretary may be made between 10 a.m. and 5 p.m. on that day.

Officers of the School:—Prof. Dunstan, M.A., F.I.C., Chemistry (Dean); Prof. Atfield, Ph.D., F.R.S., F.I.C., Practical Chemistry; Prof. Green, M.A., B.Sc., F.L.S., Botany; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy; Mr. Henry George Greenish, F.I.C., F.L.S., Materia Medica.

Entries may be made for single classes. A bench in the chemical laboratories can be engaged at any time for any number of hours daily or days weekly for any period. Students are recommended to join the Lecture classes on Chemistry and Physics in October, but other convenient periods are the beginning of January or the commencement of the Second Course in April. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance on the Courses of Pharmacy also are accepted by the conjoint Board.

For Prospectuses, &c., apply to Mr. F. W. Short Secretary to the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Demonstrator.—A. W. Warrington, M.Sc. (Vic.), F.I.C.

The College is open to male and female students above the age of sixteen years. The Session commences on Thursday, September 29, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly during the Lent and three during the Easter Term. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. For those Students who have selected Physics or Botany instead of Chemistry at the Matriculation Examination, an Introductory Course of three lectures weekly will be delivered during the Michaelmas Term. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 20, and

exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, George McGowan, Ph.D., F.R.S.E. Assistant Lecturer in Agricultural Chemistry, C. F. Archibald.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. Assistant Lecturer and Demonstrator, R. W. Stewart, B.Sc. The Session opens October 4th, 1892. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £1 1s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, and Zoology Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for two years of the three years' degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—E. P. Perman, D.Sc., F.C.S.

The Session commences October 3rd, and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 90 lectures in continuation of the Junior Course, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee £3 3s.

The Senior Course includes some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

An Elementary Organic Course of 10 lectures, and a course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Professors Thompson and Parker are recognised by the Universities of Edinburgh, Glasgow, and Aberdeen as teachers in Chemistry and Natural History respectively, so

that registered Medical Students can spend one year of their course at the University College, Cardiff. The College is also recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London or the Medical Courses at the Universities of Edinburgh, Glasgow, and Aberdeen, may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Female Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc.

Lecturer.—Arthur Richardson, Ph.D.

The session 1892-93 will begin on October 5th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is incorporated with the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms.

Senior Course.—Three Lectures a week will be given throughout the Session.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research.

Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	13	10	7½	5
„ Two Terms ..	11	9	7½	5½	4
„ One Term ..	6	5	4	3	2
„ Month ..	3	2½	2	1½	—

Students may arrange to divide their days of laboratory work into half-days.

Photographic Chemistry.

Special arrangements can be made with regard to instruction in this subject.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc. Lond., F.R.S., F.I.C.

Assistant Lecturers.—W. W. J. Nicol, M.A., D.Sc. Edin., F.I.C., and Thomas Turner, Assoc.R.S.M., F.I.C.

Demonstrator.—Harold G. Colman, Ph.D., M.Sc. Vic. The Session will be opened on Friday, September 30th, 1892.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December,

and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, Wednesday, and Thursday at 9.30 a.m. Fee, £1 11s. 6d.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once or twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term ..	7 guineas	4½ guineas.
Two Terms ..	13 „	8½ „
Three Terms ..	18 „	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course. A more advanced course upon selected subjects is also given by Mr. Turner, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Professor.—Christopher Rawson, F.I.C., F.C.S. (temporarily, until the appointment of successor).

Demonstrator.—E. E. Milnes, F.C.S.

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 12th and terminates on July 7th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters,

technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—James Hendrick, B.Sc. Lond., A.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry.—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer in Agricultural Chemistry.—Herbert Ingle, F.I.C.

Demonstrator.—C. F. Baker, Ph.D., B.Sc.

The Session begins October 10, 1892.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 11.30 p.m. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Wednesday and Friday at 9.30 a.m. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—Saturdays, from 10.30 to 12.30, from October to end of March.

Practical Course in Sanitary Chemistry.—On Tuesday and Thursday, from 2 to 5, from April to July.

Practical Organic Chemistry for Medical Students.—On Mondays, from 11 to 1, from April to July.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 14. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.I.C.

Lecturer.—L. Liechti.

Assistant Lecturers.—W. M. Gardner and J. B. Shaw.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Lecturer.—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, microscopy, leather manufacture, and practical work in the Leather Industries Laboratory.

Agricultural Department.

Professor.—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry.—C. A. Kohn, B.Sc., Ph.D.

Demonstrators and Assistant Lecturers.—C. A. Kohn, B.Sc., Ph.D., T. L. Bailey, Ph.D., and A. F. Fryer, B.Sc. *Assistant.*—H. H. Froysell.

The Session commences October 1st.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course D.—Physical Chemistry. One Term. Fee, £1.
Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Course F.—Technological Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. (8) Spectroscopy.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Special Revision Class. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Two Terms, Six Months.	Three Terms One Session.
One day	£4	—	£8
Two days	6	—	10
Three days	8	—	12
Four days	9	12	15
Five days	10	14	18
Six days	—	—	20

Technological Curriculum.

Preliminary Year.—Chemistry, either the Elementary Course or Course A, according to the previous knowledge of the Student. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Engineering Drawing and Design (in this or one of the following years). French or German. Or the Course for the Preliminary Examination, Victoria University, may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German; Intermediate B.Sc. Examination may be passed. Engineering, First Year Course, Autumn and Lent Terms.

Second Year.—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc. Pass Degree may be taken.

Third Year.—Courses D and F; part of Course C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

Evening Classes.

Lectures will be given on Metallurgy, on the Chemistry of Photography, and on Practical Chemistry with Exercises.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, and a Sheridan Muspratt Exhibition of £25 for one year, will be awarded in December, 1893, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

**DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.**

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Lecturer in Chemistry.—Saville Shaw, F.C.S.

Lecturer in Agricultural Chemistry.—R. Greig Smith, B.Sc. (Edin.), F.C.S.

Assistant Lecturer and Demonstrator.—F. C. Garrett, M.Sc. (Vid.), F.C.S.

The Session will commence on September 26th, 1892.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11.15 a.m., and will commence on Wednesday, October 5th. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays and Fridays, 3 to 4 p.m., during Michaelmas and Epiphany Terms.

3. *Organic Chemistry.*—A Course of about ninety Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Thursday, October 6th. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 10th. Fee, £1 1s.

Metallurgy and Assaying.—A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

A Lecture Course in Agricultural Chemistry will be

given on Wednesdays and Fridays from 12 to 1. Fee, Two Guineas.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week, £5 5s. per term; three days, £3 3s. per term, £8 8s. per session; two days, £2 2s. per term, £5 5s. per session; one day per week, £1 11s. 6d. per term, £3 3s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.
2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in three, at least, of the five subjects,—Mathematics, Physics, Chemistry, Geology, and Biology,—in an examination, to be held at the beginning of his second year.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 29th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE,

VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers.—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; and S. H. Davies, B.Sc.

Lecturer in Dyeing and Printing.—Ernest Bentz.

Assistant Lecturer in Metallurgy.—Gilbert J. Fowler, M.Sc.

The Session begins on October 4, 1892, and ends on June 23, 1893.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (Honours).—Mondays, Wednesdays, and Fridays, 9.30, during the Session.

History of Chemistry and Chemical Philosophy.—Wednesdays, 10.30, during the Session.

METALLURGY.—*Lectures:* The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical:* Saturdays, 9.30. The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in three years. The Degree of B.Sc. with Honours in Chemistry can also be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Scholarships, &c., are available to students.

Technological Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of Coal Tar.

Fourth Course.—Natural and Artificial Dye-stuffs.

Fifth Course.—Calico-printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Honours Course on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

A combined Lecture and Laboratory Course on the Bleaching, Dyeing, and Printing of Cotton Fabrics is given on Saturdays, at 3, by Mr. Bentz.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENT OF CHEMISTRY, METALLURGY,
AND AGRICULTURE.

Professor of Chemistry.—Frank Clowes, D.Sc. Lond., F.I.C.

Demonstrators of Chemistry.—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., and R. L. Whiteley, F.I.C.

Lecturers.—J. B. Coleman, F.I.C.; R. L. Whiteley, F.I.C.; C. Haydon White, M.R.C.S.; J. W. Carr, M.A.; F. R. Sargeant; and M. J. R. Dunstan, M.A.; F.R.S.E.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1892-93 will be as follows:—First Term, October 10th to December 24th; Second Term, January 16th to March 30th; Third Term, April 17th to July 1st.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day except Saturday and Thursday from 10 to 5, on Thursday from 10 to 1, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees: For one term, £7; for the session, £18; for day students for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

A **Pharmaceutical Curriculum** extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), Practical Dispensing, taught by demonstrations and practical work in the laboratory, and Lecture and Laboratory Instruction in Physics.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An **Agricultural Course** of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land

surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Noths, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc. F.C.S.

Demonstrators and Assistant Lecturers.—L. T. O'Shea, B.Sc., F.C.S., and G. Young, Ph.D.

The Session will commence on October 1st.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Thursday, from 10 to 11 a.m. Fee, £3 3s.

Second Year's Course.—Chemistry of Metals. Tuesday, Wednesday, and Thursday, from 10 to 11 a.m. £3 3s.; or for the First and Second Courses, £5 5s.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

(UNIVERSITY OF ST. ANDREWS).

Professor.—Percy F. Frankland, Ph.D., B.Sc., F.R.S., &c.

Assistant Lecturers and Demonstrators.—F. J. Hambly, F.C.S., and J. R. Appleyard, F.C.S.

The tenth session of the College will be opened on October 18th, 1892.

The Lectures and Laboratory practice in this University are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the Universities of Edinburgh, Glasgow, and Aberdeen.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: General Chemistry (Non-Metals, Metals, and Elements of Organic Chemistry) (100 lectures), Monday, Tuesday, Wednesday, Thursday, and Friday, from 10 to 11 a.m.; fee, £3 3s.

Second year's lecture course: 1. Advanced Inorganic Chemistry, including modern Chemical Theory (50 lectures). 2. Organic Chemistry (50 lectures). Fee for the whole course, £3 3s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory and Dyehouse. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also arranged for students preparing for their medical and pharmaceutical examinations. A three months' course of practical instruction in Sanitary Chemistry for the B.Sc. Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 2 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction are given in Chemistry, Dyeing, and Bleaching.

Forster Research Scholarship.

This scholarship, of the value of £30, is awarded annually to the best student on the condition that he devotes himself during the ensuing year to original research in the College Laboratory.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor.—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Assistants.—J. Gibson, Ph.D.; L. Dobbin, Ph.D.; H. Marshall, D.Sc.; J. Walker, Ph.D., D.Sc.; Theodore Rettie, B.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. A class for advanced students is held in summer: it meets thrice weekly; fee £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on special subjects, such as Chemical Theory, Physical Chemistry, or some particular branch of Organic and Inorganic Chemistry. These lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Winter Session, £10 10s.; Summer Session, £6 6s.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. (In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.)

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects:—1. Mathematics. 2. Natural Philosophy. 3. Astronomy. 4. Chemistry. 5. Human Anatomy, including Anthropology. 6. Physiology. 7. Geology, including Mineralogy. 8. Zoology, including Comparative Anatomy. 9. Botany, including Vegetable Physiology. Chemistry in this examination includes Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), and Simple Quantitative Determinations (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Professor.—W. H. Perkin, Jun., Ph.D., F.R.S.

Assistant Professor.—Arthur W. Bishop, Ph.D.

Demonstrator.—Bertram Prentice.

The Session begins October 1st, 1891.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is at present mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and

study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of salts, and with the tests employed in identifying these. After a careful study of the reactions of the principal metals and acids, he passes on to a complete course of the systematic qualitative analysis of simple salts and mixtures, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric and volumetric), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely Chemical or of a Technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Copies of the Calendar for 1892-93 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry.—T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 18th. A Competitive Examination, open to intending Students of Arts or Science, for a number of Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on the 13th, 14th, and 15th of October. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a Course of Laboratory Practice of two hours per week, to which Members of the Class are admitted without additional fee.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the more advanced General Principle and Theory of Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—

(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on two days of each week after May 1st. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—Advanced and Organic Chemistry.—Lectures on these subjects are given during the first or second terms, or from May 1st until the middle of July, as may suit the convenience of the class.

III.—Practical Chemistry.—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—Laboratory Pupils.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

QUEEN'S COLLEGE, CORK.

Professor.—Augustus E. Dixon, M.D.

Assistant.—D. J. O'Mahoney, F.C.S.

Systematic Chemistry.—*Inorganic:* General Principles of Chemistry. History of the chief non-Metallic and Metallic Elements and their Compounds. Periodic Law *Organic:* Classification and General Principles. Saturated, Unsaturated, and Aromatic Hydrocarbons, and their Derivatives. Chemistry of Special Animal and Vegetable Products. Organic Analysis. Determination of Vapour Density.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

Practical Chemistry.—The Course of Practical Che-

mistry consists of about thirty-nine Lectures, and will commence at the beginning of the second term.

Fee for each Sessional Course, £3.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor.—Alfred Senior, Ph.D., M.D., F.I.C.

The College Session is divided into three terms. The First Term extends from October 18 to December 24, the Second Term from January 9 to April 25, and the Third Term from April 10 to June 13.

The study of Chemistry is pursued throughout the Session by means of experimental lectures and by practice in the laboratory, where each student works independently. Attention is also directed to those technical applications of the science which the wants of the students or the special needs of the West of Ireland appear to demand.

Theory of Chemistry.—(1) A General Course of about seventy lectures is given in the First and Second Terms, embracing inorganic and organic chemistry, the non-metallic elements, the atomic theory, the metals, and the synthesis and properties of the more important fatty and aromatic compounds and their probable constitution. (2) A Special Honour Course of about twenty lectures is given in the Third Term. This course is devoted chiefly to organic synthesis, and includes a review of some of the latest researches.

Experimental Work.—(1) A General Course of about forty lessons of two hours each is given in the laboratory in the First and Second Terms, embracing the elements of qualitative analysis and the chemical examination of urine. (2) Special Courses of experiments in volumetric and gravimetric analysis, in inorganic and organic preparations, and in the applications of chemistry to medicine and the arts are arranged to meet the requirements of the students.

For prospectuses and further particulars apply to the Registrar.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN.

(SCIENCE AND ART DEPARTMENT).

Professor of Chemistry.—W. N. Hartley, F.R.S.

Assistant Chemist.—Hugh Ramage, A.I.C., Associate of the Royal College of Science.

The Session commences on Monday, October 3rd, 1892, and ends on June 22nd, 1893.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry, (2) Chemical Manufactures, (3) Metallurgy, (4) Analytical and Experimental Chemistry, (5) Instructions in Chemical Research.

Fees payable by Associate Students in the Faculty of Manufactures:—For the entire Course—first year, £13; second year, £23; third year, £14.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

The following are supplementary courses of instruction for beginners:—

Laboratory Instruction in the Theory of Chemistry. A two-months' Course. By arrangement with the Professor the hours of attendance are fixed so as to suit, as far as possible, the convenience of the students, the laboratory accommodation being limited.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—*Central Institution, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given in this Institution is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Monday, Sept. 19th, and the Winter Session opens on Wednesday, Sept. 28th.

Technical College, Finsbury.—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments:—1. Mechanical Engineering and Applied Mathematics; 2. Electrical Engineering and Applied Physics; 3. Industrial and Technical Chemistry; 4. Applied Art; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 27th, 1892, and the work of the Session will commence on October 4th.

ADDEY'S SCIENCE AND ART SCHOOL, Church Street, Deptford.—Head Master, William Ping, F.C.S.—Day

and Evening Classes in Theoretical and Practical Chemistry, &c.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREAM'S BUILDINGS, CHANCERY LANE.—*Chemistry*: Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry*: Mr. G. Chaloner, F.C.S. Lectures—Elementary, Tuesdays, 8.30 p.m.; Advanced, Thursdays, 7 p.m.; Practical, Tuesdays, 6—8 p.m.; Thursdays, 8—10 p.m.; Saturdays, 7—9 p.m. *Organic Chemistry*: Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6.30 p.m.; Practical, Wednesdays, 7.30 p.m., Fridays, 6 p.m.

THE CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., and Mr. Lionel Cooper. Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

THE CITY SCHOOL OF CHEMISTRY AND PHARMACY, 27, Chancery Lane, London, W.C.—Principal, Mr. Maurice Williams. Assisted by Mr. T. A. Ellwood, A.I.C., F.C.S., Mr. Martin J. Cole, and Mr. E. Hayward. Theoretical and Practical Chemistry, Chemical Physics, Theoretical and Practical Pharmacy, Materia Medica, Botany, Prescription Reading, Microscopy, &c.

MIDDLESEX COLLEGE OF CHEMISTRY AND PHARMACY, 40, Charlotte Street, Portland Place.—Principal, F. H. Painter. Day and Evening Classes and Laboratory Instruction in Chemistry, Pharmacy, Materia Medica, &c.

PENYVERN HOUSE MILITARY AND ENGINEERING COLLEGE, Penyvern Road, Earl's Court, S.W.—Lecturer on Chemistry, T. G. Nicholson, B.Sc., F.C.S. The courses of instruction are arranged to suit the requirements of Students preparing for entrance into the various branches of the public service; Students working for scholarships at the Universities and Hospitals; engineering students preparing for entrance into the Royal Engineering College, Cooper's Hill, the Central Institution, or the Royal College of Science at South Kensington, and into engineering works. Arrangements are also made to suit the requirements of persons desirous of working at special subjects in the Physical and Chemical Laboratories.

SOUTH LONDON SCHOOL OF PHARMACY, 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £12 12s.; afterwards £3 3s. per month respectively, inclusive of all departments.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemical Department, Mr. A. G. Bloxam, F.I.C. Lectures and Practical Classes, also special classes in Chemistry as applied to various arts and industries, are held in the evenings from 7.30—10.0, and are open to both sexes.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Lecturer, Mr. D. S. Macnair, Ph.D., F.C.S.; Assistant, Mr. F. G. Pope. The classes are open to both sexes without limit of age. Evening classes in Theoretical and Practical Chemistry.

POLYTECHNIC INSTITUTE, 309, Regent Street, London,

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UNIVERSITY TUTORIAL COLLEGE (the Science Department in London of University Correspondence College).—During the past session the number of Science students so greatly increased that with the new academic year extensive laboratories will be opened in Red Lion Square, Holborn, W.C. They will accommodate over 100 students and will be fitted according to the requirements of modern Science teaching.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E.—Messrs. Wills and Wootton. Day and Evening Classes.

ARTILLERY COLLEGE, WOOLWICH.—Chemistry and Physics, Dr. W. R. E. Hodgkinson, F.R.S., &c. Metallurgy, H. Bauerman, F.G.S.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

THE CLIFTON LABORATORY, Berkeley Square, Bristol.—Principal, Mr. Ernest H. Cook, D.Sc.Lond., F.I.C., F.C.S.; Assistants, Messrs. H. J. Palmer, F.C.S., S. B. Froude, and E. H. Read. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations.

LEEDS SCHOOL OF SCIENCE AND TECHNOLOGY, (Mechanics' Institution, Leeds).—Lecturer on Chemistry, Mr. S. J. Harris, M.Sc., F.C.S. Lecturer on Metallurgy, Mr. B. A. Burrell, F.I.C., F.C.S. Lecturer on Physics, Mr. A. Wheatley, B.Sc. The Chemical Laboratory is open for five evenings, and the Metallurgical Laboratory for two evenings per week. There is a three year's course of lectures in Inorganic Chemistry, and a two year's course in Organic Chemistry and Metallurgy. The course of Practical Work in Chemistry includes Organic Synthesis.

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool (A. Norman Tate and Co.).—Principal, Mr. F. H. Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

THE MUNICIPAL TECHNICAL SCHOOL, Princess Street, Manchester.—Mr. J. H. Reynolds. Day and Evening Classes.

SHEFFIELD BOROUGH ANALYSTS' LABORATORY, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

STOCKPORT TECHNICAL SCHOOL.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. Lecturer on Chemistry and Metallurgy: Mr. G. W. Davies, F.C.S. Lecturer on Dyeing and Hat Manufacture: Mr. W. M. Gardner, F.C.S. Theoretical and Practical Instruction is given in Chemistry, Metallurgy, Dyeing, Bleaching, and Hat Manufacture. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application.

TECHNICAL INSTITUTE, SWANSEA.—Classes in Theoretical and Practical Inorganic Chemistry and Metallurgy, Electricity, &c., from October to May. Principal, W. Morgan, Ph.D., F.C.S., F.I.C.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1712.

EXPERIMENTS ON FLAME.*

By ARTHUR SMITHELLS, B.Sc.

THE author began by describing four distinct regions of an ordinary luminous flame, the existence of which he thought could not be denied by any impartial observer. His experiments had arisen from a desire to understand more fully the chemical changes which determined this peculiar structure, and especially the twofold character of the outer sheath. He described the construction and demonstrated the use of his apparatus for separating the two cones of combustion in non-luminous flames, and gave a summary of the results he had obtained with it. He considered these results to furnish fresh proof that when a hydrocarbon is starved of oxygen the carbon will burn more readily than the hydrogen, and that accordingly the luminosity of ordinary flames must not be explained, as is often done, by assuming the very reverse of this. The luminosity of ordinary flames is now generally admitted to be due to the separation of solid carbon in the flame, and this must be ascribed to a decomposition or dissociation of the hydrocarbons by heat. This heat is supplied by the sheath of non-luminous combustion surrounding the flame. The author considers this sheath, which consists of two parts (a barely visible outer part and a bright blue inner one), to correspond to the two cones of combustion in a non-luminous flame. The author, whilst admitting from the result of experiments made by Prof. Lewes and by himself that acetylene was present in the interior of luminous flames, thought that Prof. Lewes had not established his view that luminosity was mainly and essentially due to the formation and subsequent dissociation of acetylene, and that he was altogether relying too much upon that substance. A study of the precise cause of carbon separation was being undertaken by the author with the aid of his flame-cone separator, a single hydrocarbon (ethylene) being employed. Other experiments with the flame-cone separator relating to the spectra of metallic salts were exhibited. The chief conclusion was that the spectra obtained when metallic salts were introduced into non-luminous flames were the outcome of and were dependent upon chemical changes.

Sir GEORGE STOKES, referring to the latter portion of Prof. Smithells' paper, said he believed that he was to some extent in agreement with the author, but that there was one point of difference. He accepted the view that spectra obtained in flames may be due in an important degree to the heat developed during the chemical reaction. He was of opinion, however, that the particular radiations produced must be ascribed not to the act of combination, but to the consequences of that act in setting up a vibration of the newly formed substance. He attributed the phenomena, in fact, to the child of the reaction and not to the parents. He had explained his views on the subject to Prof. Smithells in the course of correspondence, and he would only now say that he found insuperable difficulty in ascribing the absorption spectrum of sodium to chemical action.

With reference to the luminosity of flames he considered it established beyond question that this was due to solid matter. He described the optical proof which he and

others had adduced. He understood from Professor E. Frankland that the latter had abandoned the view that luminosity was due to dense hydrocarbon vapours.

Sir HENRY ROSCOE agreed with Sir George Stokes that there would be great difficulty in explaining absorption spectra on the hypothesis put forward. He was, however, of opinion that it was not unnatural to ascribe some effect to the disengagement of heat during chemical reactions, and he thought that it would be difficult if not impossible to explain some of the experiments which had been shown on any other assumption.

Mr. THOMAS alluded to the experiments which he had performed a good many years ago on the combustion of hydrocarbons with restricted amounts of oxygen during a study of fire-damp explosions. He had shown that carbonic oxide and free hydrogen were produced in such cases, but he was inclined to ascribe this not to the prior combustion of the carbon but to the combustion of part of the gas to carbon dioxide and water, and the subsequent action of those substances on the residual hydrocarbon.

Prof. LIVEING expressed general concurrence with the view that chemical action had an effect in the production of spectra, and he alluded to some unpublished experiments by Prof. Dewar and himself on the absorption spectrum of liquid oxygen, in which phenomena were observed that he could only ascribe to the action of oxygen molecules on each other. With regard to the luminosity of flames he thought that Prof. Frankland had no need to abandon the view that it might be due to hydrocarbons, though undoubtedly the hydrocarbons were solid in the flames. He, the speaker, had found it impossible by any process to deprive carbon separated from flames, of the hydrogen which it always contained, and which he therefore thought to be in a state of chemical combination with the carbon.

Prof. RAMSAY said he agreed with Prof. Smithells up to the hilt. He had lately found that with perfectly pure sodium in a vacuum tube it was impossible to get any trace of the D line.

Prof. LEWES, in reply to the discussion, said that he felt sure of the facts that he had stated with respect to acetylene, but did not consider the subject worked out. He quite agreed with Prof. Smithells as to the impossibility of making exact analyses of mixtures of hydrocarbons, but acetylene was one of the few that could be determined with precision. He did not agree that a doubt of the readier combustibility of carbon than hydrogen was mere prejudice, and he thought that so long as the chemical changes taking place could be explained on the older views, it was unnecessary and undesirable to bring forward the theory advocated by Prof. Smithells. He was sorry if he had misrepresented Prof. Frankland's views, but he had certainly understood from that gentleman that he still adhered to his theory of luminosity being due to dense hydrocarbon vapours.

Prof. SMITHELLS, in reply, wished to clear himself of a suspicion of having brought forward revolutionary and unnecessary theories. As a matter of fact the theory he advocated, that the carbon of a hydrocarbon burnt more readily than the hydrogen, was put forth at the beginning of the century by John Dalton. Dalton's discovery had been ignored until the same facts were again discovered by Kersten. Even that was not enough to secure their acceptance by the text-book makers, and though the matter had again been independently brought to light by Ernst von Meyer and Thomas, he (the speaker) had once more to discover it, and endeavour to put it forward in place of what Prof. Lewes called the orthodox idea, but what was really an idea that had been exploded at the beginning of the century.

Mr. P. J. HARTOG remarked that a crucial experiment had been performed in Prof. Dixon's laboratory. The rate of explosion of ethylene with sufficient oxygen to produce carbonic oxide had been measured, and it had been found that if the oxygen were increased beyond this

* Read before the British Association, Edinburgh Meeting, 1892, Chemical Section. The Paper of which this is an abstract and the discussion followed the Paper read by Prof. Vivian Lewes and published in the CHEMICAL NEWS, vol. lxxi., p. 99.

the velocity of explosion was diminished, the extra oxygen acting merely as a diluent. This clearly proved that the carbon first burnt to carbonic oxide.

Prof. LEWES said this was the first fact that he had heard which appeared to him in any degree of a decisive character in favour of the readier combustibility of carbon.

The PRESIDENT conveyed the thanks of the meeting to the readers of the papers.

NOTE ON

SOME ALLOYS OF IRON, ALUMINIUM, AND MANGANESE.*

By T. W. HOGG.

THE alloys which form the subject of this short paper were prepared by mixing ferro-manganese with aluminium, both previously fused. These alloys possess the unexpected feature of being readily attracted by the magnet, and it is principally on this account that they have been thought sufficiently interesting to bring before the members of this section, especially as the alloys of aluminium have for some time been attracting much attention.

It is now well known that the addition of manganese to iron or steel produces an alloy which is not attracted by the magnet, alloys containing 8—12 per cent of manganese being only feebly magnetic, and over this proportion they may be said to practically have no influence on the magnet at all.

Aluminium also possesses a similar property, but in a less marked degree. Ferro-aluminium containing 13 per cent Al is still readily attracted, and it is not until the alloy contains about 20 per cent Al that the effect here alluded to takes place.

It is therefore an interesting fact that the addition of aluminium to a ferro-manganese alloy, which of itself would be quite inert, becomes readily attracted. In one of the alloys here shown the aluminium is only present to the extent of 3.05 per cent, and although it contains only 14.80 per cent iron, it responds to the influence of the magnet almost as readily as a piece of iron.

With regard to the disintegrated alloy the effect is still more remarkable, as we have present not only manganese but also a sufficient quantity of aluminium itself to destroy the influence of the magnet; yet instead of acting together in the same direction they have done exactly the reverse, and here again, although the proportion of iron is small, the magnet attracts it readily.

The alloys which I have here alluded to were the result of an experiment made to ascertain the possibility of forming a reliable homogeneous alloy of aluminium with ferro-manganese, and for this purpose 50 lbs. of ferro-manganese containing 82 per cent Mn, and 5.56 lbs. of aluminium containing 99.5 per cent Al, were separately melted in large crucibles. After perfect fusion the ferro-manganese was poured into the aluminium; after stirring for about half a minute the mixture showed such decided signs of becoming pasty that it was at once poured into an ingot mould. After about two-thirds had been poured the remainder suddenly solidified and was roughly knocked out of the crucible. The alloys presented no apparent dissimilarity, and it was not thought worth while to examine them until after keeping for about three months, when the portion which had solidified in the crucible commenced to fall into pieces in the same way that high percentage ferro-manganese (85 per cent Mn) is known to do, and this action has gone on until after twelve months it has completely disintegrated and is now in the condition of the specimen shown.

The analyses of the two portions showed a remarkable

difference in composition. The disintegrated portion contains:—

Iron	10.80
Manganese	54.86
Carbon	2.32
Aluminium	25.34
Silicon	0.79
Sulphur	traces
Phosphorus	0.107
Copper	0.075

94.292

This analysis was repeated with practically the same results; the deficiency is no doubt due to oxygen, slight oxidation having taken place owing to the finely-divided condition of the alloy. It has a specific gravity of 3.61.

The examination of the portion which was poured off showed it to have a specific gravity of 6.12, and that it contained:—

Iron	14.80
Manganese	75.40
Carbon	5.55
Aluminium	3.05
Silicon	0.886
Sulphur	traces
Phosphorus	0.184
Copper	0.075

99.945

This alloy has not altered its condition since it was made, there being no signs of disintegration. Whether this difference in composition between the two alloys is the result of the great difficulty of mixing aluminium with the heavier metals, or has been produced by separation, is not quite clear, if the carbon may be taken as an indication; it seems to show not only separation but also actual loss of this element.

A QUICK METHOD FOR REFINING GOLD, SILVER, AND PLATINUM IN QUANTITY.

By H. N. WARREN, Research Analyst.

THE following note refers principally to the refining of standard silver, gold, and dental alloy, or other such commercial metalliferous products containing the precious metals. It not unfrequently happens that in assay offices where these metals are purchased in large quantities that before rendering them fit for the market a separation of each is required. The gold alloys are in this case melted and further alloyed with two and a half times their weight of standard silver, the alloy thus obtained parted by the aid of nitric acid, the amorphous gold remaining dried, after washing, and granulated. The solution containing the silver as nitrate freed from the same by the introduction of copper bars, the precipitated silver washed, dried, and melted, being either cast into bars or granulated as required, the copper being afterwards replaced by iron in order to serve for a further operation.

Dental alloy—that is, silver alloyed with from 25 to 30 per cent of platinum—presents a more difficult problem. Platinum alloyed with a sufficiency of silver is soluble in nitric acid; but in this case about 10 per cent of that metal passes into solution after long boiling with the same, the whole of the silver in the meantime becoming dissolved. To the solution containing the platinum as nitrate is introduced also a bar of copper; the whole of the platinum, together with the silver, are thus quickly replaced, the silver being afterwards re-dissolved by the addition of a further quantity of nitric acid, leaving the platinum untouched, which is now returned to the first portion, and the whole dissolved by the addition of *aqua*

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

regia, precipitated by an excess of ammonium chloride, evaporated to dryness, and ignited, leaving pure platinum.

The precipitation of silver as chloride in presence of platinum is useless, as it carries down with it nearly a quarter of the platinum present.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

DISCOVERY OF HEXA-iodo-BENZENE.

By G. E. SHAW.

IN attempting to prepare *p*-di-iodo-benzene by Ystrati's method (*Bull. Chem. Soc.* [3], v., p. 158), 250 grms. iodine were heated with 100 c.c. pure benzene and 200 c.c. strong HSO_4 a few hours daily for ten days. A mixture was obtained from which, besides mono- and di-iodo-benzene, another compound was easily separated by its comparative insolubility in alcohol and benzene. By crystallisation from CS_2 , after treatment with animal charcoal, about 20 grms. were obtained in white needles containing only C and I. Two estimations of the iodine gave (1) 89.99 per cent, (2) 91.10 per cent; agreeing with the formula C_6I_6 , 91.33 per cent I. Its melting-point (corrected) is 248°C . Aniline and nitrobenzene are the only solvents in which it freely dissolves. Baeyer (*Ber.*, xviii., p. 2275), obtained a white substance soluble in alcohol and melting at 184°C . by heating di-iodo-acetylene on a water-bath, and which he supposed to be C_6I_6 , but gives no analysis. If hexa-iodo-benzene was really formed at all it must have been very impure.

Finsbury Technical College, Aug. 23, 1892.

ON THE DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

(Continued from p. 115).

The Influence of Temperature on the Colour Effects of Salt Solutions.

IN addition to determining the effects of dilution on salt solutions, the effect of temperature was also tried. Generally, 30 c.c. of the solution was taken, and this was first compared, merely as a test for the correctness of colour judgment, with some of the solution of the same concentration, both solutions being at 20°C . The value found generally agreed to within 0.5 c.c. The tube containing the solution was then placed in a water-bath and heated to from 62° to 63° . It was then compared as to colour with the original solution, the radiation between the two tubes being stopped by placing a thick piece of cardboard between them. The short time necessary for the comparison was just enough for the solution to cool to 60° , or to within half a degree of this temperature. The temperature of the solution was again taken immediately after the comparison had been made to verify this. The solution was then allowed to cool to 52° , when it was again compared, then to about 41° , then to a little above 30° , and lastly it was compared again at 20° in case any change may have taken place in the solution caused by the heating, as was found to be the case with one or two ferric salts. It was scarcely possible to make comparisons at temperatures much above 60° , as the solution then began to give off enough aqueous vapour from its surface to produce a cloudiness in the tube.

Salt.	Dilution in litres.	Colouration at—			
		30° .	40° .	50° .	60° .
Cupric sulphate ..	1	102.6	106.1	111.3	116.5
" ..	10	104.7	109.1	112.5	115.7
" ..	100	104.9	106.2	110.6	113.8
" chloride ..	0.4	112.5	118.3	123.3	—
" ..	10	104.1	106.7	109.5	113.6
" ..	100	105.4	110.1	113.1	117.1
" nitrate ..	1	102.3	104.6	105.9	108.2
" ..	10	103.4	107.5	110.6	112.2
" chlorate ..	1	101.8	103.7	106.7	109.8
" ..	10	105.9	112.5	115.6	119.5
" acetate ..	2.5	107.2	122.9	133.1	145.2
" ..	10	109.8	119.1	128.6	138.7
" ..	100	105.3	117.1	122.1	129.2
Nickel sulphate ..	1	101.9	106.2	107.5	108.7
" ..	10	101.9	106.2	108.5	111.8
" chloride ..	1	104.7	108.5	115.6	122.7
" ..	10	101.6	105.8	114.8	118.8
" nitrate ..	1	102.4	104.9	108.5	—
" ..	10	103.7	105.4	108.4	113.9
Cobalt sulphate ..	1	105.0	114.3	126.1	141.2
" ..	10	109.7	117.4	130.3	—
" ..	100	103.9	107.9	116.8	—
" chloride ..	1	113.9	122.6	136.5	142.6
" ..	10	107.7	111.9	117.3	125.0
" ..	100	105.8	108.1	113.0	116.6
" nitrate ..	1	111.5	128.3	143.3	170.0
" ..	10	105.7	110.1	118.0	126.3
" ..	100	102.1	103.7	106.7	110.7
Uranyl sulphate ..	2.5	103.5	108.7	113.0	120.9
" ..	10	106.5	116.2	123.1	131.3
" ..	100	102.8	108.7	115.7	121.6
" chloride ..	2.5	112.3	122.9	133.6	145.1
" ..	10	105.5	113.9	129.1	137.5
" ..	100	106.6	113.7	117.5	124.6
" nitrate ..	2.5	111.1	122.2	134.2	139.3
" ..	10	104.1	111.3	118.5	122.3
" ..	100	105.5	111.5	116.9	121.4
" acetate ..	2.5	106.4	113.7	121.7	134.6
" ..	10	104.0	108.6	116.9	121.3
Chromium sulphate ..	10	—	—	—	100
Chrome alum ..	10	113.4	123.2	134.8	142.0
Chromium chloride ..	10	—	—	—	100
" nitrate ..	10	—	—	—	100
Potassium chromate ..	1	127.1	162.0	188.5	204.8
" ..	10	115.0	148.1	187.3	237.7
" ..	100	110.1	116.0	132.1	146.8
" ..	1000	103.2	105.5	113.6	121.5
" bichromate ..	10	118.7	137.1	151.2	164.9
" ..	100	106.1	116.8	129.1	143.1
" ..	1000	105.1	115.6	122.0	—
Chromium trioxide ..	1	111.6	128.5	150.6	176.6
" ..	10	108.3	124.8	141.0	151.6
" ..	100	104.6	108.8	118.9	125.9
" ..	1000	100	100	100	100
Ferric chloride ..	1	116.4	134.8	154.0	171.1
" ..	10	127.9	155.9	200.1	248.9
" + HCl ..	1	136.4	188.3	236.0	256.9
" ..	10	174.7	286.4	—	—
" acetate ..	10	105.3	117.1	122.4	130.3
" oxalate ..	5	107.7	114.2	126.9	140.4
" ..	100	124.4	145.4	175.2	199.6
" tartrate ..	10	112.9	125.4	140.2	168.7
" ..	100	117.6	126.5	150.2	—
" citrate ..	5	112.8	123.8	134.9	157.5
" ..	100	104.2	109.6	112.3	125.1
Ferric citrate + citric acid ..	10	105.7	112.3	120.7	129.5
Ferric citrate + citric acid ..	100	106.9	119.0	129.7	141.7
Ferric citrate + citric acid ..	1000	102.1	104.0	105.7	110.7
Ferric ammonium citrate ..	100	—	—	—	103.3

Salt.	Dilution in litres.	Colouration at—			
		30°.	40°.	50°.	60°.
Ferric ammonium citrate	1000	104.1	105.1	107.6	108.3
Ferrous citrate	100	111.6	115.4	119.8	124.5
Potassium ferrocyanide	1	108.2	116.4	127.6	139.4
Potassium ferrocyanide	10	103.8	107.6	113.3	123.2
Potassium ferridcyanide	1	—	—	—	106.0
Potassium ferridcyanide	10	—	—	—	105.1
Potassium ferridcyanide	100	—	—	—	103.6
Potassium permanganate	1000	—	—	—	103.3
Potassium permanganate	10000	—	—	—	100
Iodine	100	—	—	—	100

Of copper salts, the sulphate shows a moderate increase of colour with rise of temperature, the increase being about the same for the normal and decinormal solutions, and slightly less for the centinormal. Cupric chloride shows about twice as great an increase in its most concentrated solution as the sulphate does, but in the decinormal and centinormal solutions it falls to about the same value. The cupric chloride solutions were very difficult to compare accurately, as they change colour so greatly on heating. Thus no colour comparisons could be made with the normal solution, as it is blue at 20°, but quite green at 50° or 60°. Cupric nitrate solutions show less increase in colour on heating than any other cupric salts. The normal cupric chlorate solution comes next. In both cases, but especially with the chlorate, the 10 litres solution shows considerably greater increase than the normal solution. Solutions of cupric acetate show greater increase in colour than any other copper salts, the 2.5 litres solutions showing the greatest increase, then the 10 litres, and then the 100 litres solution. Nickel salts show a similar increase to the copper salts, the chloride showing the most increase, and the sulphate and nitrate possessing almost identical values. With all the nickel salts at all dilutions, the solutions were considerably more yellowish in tinge at the higher temperatures than at the lower. Cobalt salts show considerably greater increase on rise of temperature than either copper or nickel salts. With the 10 litres and 100 litres solutions of the sulphate, colour comparisons could not be made at 60°, as a slight decomposition set in, and they became milky. Like the solutions of the chlorides of copper and nickel, that of cobalt shows a much greater increase for the 1 litre solution than for the 10 litres, while this again is greater than for the 100 litres solution. The nitrate of cobalt shows a similar behaviour, only to a more marked extent. Cobalt nitrate acts quite differently from the nitrates of either copper or nickel. All the cobalt solutions were more purple in tinge in the hot solutions than in the cold; this was especially the case with the nitrate.

Uranyl salt solutions, taken as a whole, show considerably greater increase in colour effect on heating than those of either copper or nickel salts, their values, in fact, approaching to those of cobalt salts. Unlike these salts, however, there is not nearly so great a difference between the values or the solutions of different concentrations. The chloride, like cupric, nickel, and cobalt chlorides, shows the greatest increase in its concentrated solution and the least increase in its most dilute. The nitrate also acts in the same way. It will thus be seen that, in respect of the relation of increase in colour to temperature, the uranyl salts show great resemblance to the corresponding cobalt salts.

Chromium salts, with the exception of chrome alum, act in a different manner from almost all other salts, for

they show no change of colour whatever on rise of temperature. To what this is due it is not possible to say, but it is remarkable that these salts and potassium permanganate, which likewise is scarcely at all affected by temperature, all crystallise without water of crystallisation, whilst chrome alum, whose crystals contain water of crystallisation, is affected by temperature like other salts. Also, it is doubtful whether solutions of chromium salts, except chrome alum, undergo any true decrease of colour at all on dilution, and potassium permanganate only undergoes a slight decrease at extreme dilutions. The values given for chrome alum are scarcely even approximate, as the solution becomes so green on rise of temperature that accurate comparison is impossible. At 100° chrome alum solutions become as green as chromium sulphate solutions; it can thus at this temperature contain no molecules of chrome alum as such in solution, but only chromium sulphate molecules. The change of colour was still more marked with the 100 litres solution, so that in this case no comparison could be made at all.

Potassium chromate, though crystallising without water of crystallisation, and though showing no decrease in colour whatever on dilution of its solutions, is nevertheless more affected by temperature in its solutions than almost any other salt examined. Its decinormal solution shows the greatest increase, and its millinormal the least. The same thing holds for potassium bichromate. The dependence of the amount of colour change of a salt solution on the dilution is most strikingly displayed in the case of chromium trioxide; for whilst the colour of the normal solution is almost doubled on heating to 60°, that of the millinormal undergoes no change whatever. This latter solution therefore contains the salt in such a state that it has less than half the colour effect of the concentrated solution, and is also wholly unaffected by temperature. As has been previously shown, this solution probably only contains H_2CrO_4 molecules, so the dilution must be so great that even a considerable rise of temperature is not enough to set free any molecules of CrO_3 , and so cause an increase in colour.

Ferric chloride solutions are greatly affected by temperature—the decinormal solution more than the normal. This is due to the formation of ferric oxide in the solution, for on heating the centinormal solution to 60°, it became dark reddish brown, and moreover did not regain its original colour on cooling to 20° again.

Solutions of ferric chloride containing free hydrochloric acid are much more affected by temperature than solutions of ferric chloride alone. The great increase in colour is not due to the same cause however. It has been shown how largely acid ferric chloride solution dissociates on dilution, and it was also remarked how very greatly the colour of the normal solution is changed on dilution to 5 litres, the change being from brown to yellow. Now on heating the acid ferric chloride solutions, they also change very rapidly to a more brownish colour, so much so that no colour comparisons could be made with the decinormal solution above 40°. It is clear, therefore, that on heating a solution the salt tends to change to the same condition in which it exists in its more concentrated solutions at ordinary temperatures. As, therefore, on concentrating acid ferric chloride solutions from 100 litres to 1 litre, the colour is increased to more than six times its value, the increase of colour from 100 to 256.9 on heating to 60° is not extraordinary.

Decinormal ferric acetate solution shows a moderate increase of colour on heating. More dilute solutions than this could not be examined, as they decomposed with the formation of the basic acetate. Ferric oxalate solutions showed a greater increase, especially the 100 litre solution, the colour effect of which was doubled by heating to 60°. This was evidently owing to the same cause that affected acid ferric chloride solutions, for concentrated solutions of ferric oxalate are of a yellowish brown colour, and dilute solutions of a dirty green, and these solutions, with rise of temperature, rapidly begin to turn

brownish yellow, and so the molecules of the salt in them must exist in the same state as in the more concentrated solutions.

Ferric tartrate solution showed about the same colour increase as the oxalate solution. The value for the centinormal solution could not be determined at 60°, as the salt began to decompose and the solution turned milky. Ferric citrate and acid ferric citrate solutions show similar values. Ferric ammonium sulphate solutions on heating show only a very slight increase of colour effect, and, as has been shown, this salt undergoes no change in colour on dilution, whilst ferric citrate solutions increase considerably in colour. Ferrous citrate solution shows a moderate increase in colour on heating.

The normal solution of potassium ferrocyanide shows considerably greater increase in colour than the decinormal. It would be thought that the increase for potassium ferridcyanide would, if anything, be greater than that of the ferrocyanide, but such is not the case. Potassium permanganate shows a barely perceptible increase at 1000 litres dilution, whilst at 10,000 litres it shows no change at all. Iodine solution, which exhibited such remarkable variations in colour on dilution, did not on heating show any change at all. In this respect it resembles chromium salts.

The effects of temperature on solutions of different coloured salts have thus been examined in detail; it remains for us to draw a few general conclusions from the results. In the first place it is evident that all the salt solutions may be divided into two classes, one containing solutions which increase in colour on rise of temperature; this class includes almost all the solutions examined, and the other class containing those salts which show no change of colour. There is no third class containing solutions which decrease in colour on heating. The second class contains only a very small number of solutions; they are those of chromium sulphate, chloride, and nitrate, iodine, and perhaps potassium permanganate. These substances also possess one or two other properties in common. Thus they, all of them, crystallise without water of crystallisation. Solutions of none of them show regular changes in colour effect on dilution, and only chromium sulphate, and perhaps potassium permanganate solutions, decrease in colour at all. Coloured salts may thus be divided into two moderately well-defined classes. The salt potassium chromate presents a difficulty, however; for whilst, on the one hand, it does not crystallise with water of crystallisation, and does not decrease in colour on dilution, on the other hand it suffers very great increase of colour with rise of temperature.

The increments of colour of salt solutions on heating show general relations depending on the nature of the base of the salt, on the nature of the acid radicle, and on the degree of dilution of the solution. Thus, as a general rule, ferric salts are the most affected by temperature, then cobalt and uranium salts, then copper and nickel salts, and lastly potassium ferrocyanide and ferridcyanide. Again chlorides, with the exception of cobalt chloride, show the greatest increase; nitrates, with the exception of copper nitrate, come next, and sulphates last. With regard to the dependence of colour increase on dilution, all the sulphates show the greatest increase in their decinormal solutions, a lesser increment in their normal solutions, and the least in their centinormal. All chlorides, with the exception of ferric chloride, show the greatest increments in their normal solutions, a lesser increment in their decinormal solutions, and with the exception of cupric chloride the least increment in their centinormal solutions. The nitrates do not show such a general resemblance.

The colour effects of the solutions were determined at temperatures intermediate between 20° and 60°, in order to ascertain whether the colour effect increased at a rate proportionate to the temperature, or to some power of the temperature. Such relations could only be recognised with any certainty if they were well marked, and

occurred in a considerable number of salts; for all the numbers given are liable to an error of quite 2 per cent, or even more in some cases where the tint of the solutions changes on heating, and so renders comparison more difficult. Most of the numbers agree better on the supposition that the increase of colour is directly proportional to the increase of temperature, but in some, as the concentrated solutions of cobalt sulphate and nitrate, uranyl sulphate and acetate, ferric oxalate, and both solutions of acid ferric chloride, and also in some of the solutions of potassium chromate, bichromate, and chromium trioxide, the colour effect seems to increase at a greater rate than the temperature increases.

It has been shown that when solutions of nickel salts are heated they tend to turn yellow, the colour of their anhydrous salts; cobalt salt solutions tend to turn blue, the colour of their anhydrous salts. Blue solutions of cupric chloride tend to turn green, or to the colour of their more concentrated solutions; chromium trioxide solutions tend to turn more red, the colour of solutions containing free CrO_3 molecules; acid ferric chloride solutions tend to turn brownish yellow, the colour of their more concentrated solutions, and lastly, ferric oxalate solutions tend to turn from dirty green to brownish yellow, which is the colour of concentrated solutions of this salt. Thus in every case in which concentrated solutions of a salt have a different colour from the dilute solutions, it was found that on heating these dilute solutions their colour tends to change to the colour of their concentrated solutions. It is, therefore, a general principle which probably applies to all salt solutions, with one or two exceptions, as in the case of sodium sulphate and sodium carbonate, that the action of heat on a solution of a salt is to change the condition in which the molecules of the salt exist to the same condition they exist in in a more concentrated solution. Now all colorimetric determinations which bear on the subject at all prove that in the hot or in the concentrated solutions the molecules of salts tend to change their condition to that in which they exist in the anhydrous state; hence it is another general principle probably applying equally with the other to all salt solutions, that hot and concentrated salt solutions contain the molecules of salt combined with less molecules of water than cold or more dilute solutions. This is contrary to the conclusion of S. U. Pickering (*Chem. Soc. Journ.*, March, 1890), that the composition of hydrates in solution is not changed on variation of temperature.

Colorimetric determinations are thus without exception in favour of the hydrate theory of solution.

It may be said that as salts exist in dilute solutions in the same condition as in cold solutions, and as these show less colour effect than hot solutions, may not the decrease in colour effect of a salt on dilution be due to the same cause, viz., hydrates of less colour effect being formed. The observations detailed in this paper should in this case be taken to prove merely the existence of hydrates in solutions, and should afford no proof whatever of any dissociation taking place. This cannot be said to be the case, however. If it were so then the decreasing colour effects of solutions on dilution should be exactly proportional to the decreasing colour effects of the same salts on cooling their solutions, whereas it is nothing of the kind. Thus, to take a few instances, cupric nitrate solution decreases in colour effect on dilution more than cupric sulphate solution, but on heating the sulphate solution shows the greater increase. Cobalt chloride solution on dilution decreases in colour effect more than cobalt nitrate solution, but is more affected by rise of temperature.

Potassium chromate solution, though greatly affected by temperature, suffers no change at all on dilution. Chromium trioxide solutions, which are less affected by temperature than those of potassium bichromate, decrease in colour on dilution to nearly twice the extent. At the same time it cannot be denied that there is a general

resemblance between the two series of determinations. Thus of copper salts the acetate solution shows the greatest colour decrease on dilution and the greatest increase on heating. Cobalt salts show more dissociation than most other salts; they also show more colour increase on heating. Of uranium salts the chloride is most affected by dilution, and also by rise of temperature of its solution. Acid ferric chloride solution behaves similarly. Also it may be said that chromium salts, with the exception of chrome alum, show little if any increase in colour in their solutions on heating; that they therefore do not form hydrates in solution, and that this is borne out by the fact that they crystallise without molecules of water of crystallisation.

A great objection to this is that potassium chromate solutions—the great colour increase of which, on heating, must be due to the presence of hydrates—show no decrease of colour at all on dilution. Thus it would seem possible that the colour decrease of a solution on dilution need not necessarily be even in part due to the formation of fresh hydrates of less colour effect. It is probable, however, that in most cases it is due partly to dissociation and partly to the formation of hydrates of less colour effect. How much of the effect is due to each of these causes it is not possible to say, but it probably varies greatly with solutions of different salts.

On heating salt solutions the increase is probably wholly due to the influence of hydrates, for the dissociation values of solutions do not appear to vary with temperature. The increments of colour effect on heating for different salt solutions do not appear to bear any general relations to either the solubilities of the salts in water, or to the number of molecules of water of crystallisation they crystallise with.

(To be continued.)

A SIMPLE METHOD FOR DETERMINING THE WATER IN IODINE.

By Prof. Dr. MEINECKE.

For determining the water of crystallisation in iodiferous substances readily capable of decomposition, E. Ostermeyer passes the vapours of iodine and water, by means of a current of air, through a moderately heated combustion tube filled with spirals of sheet silver or copper, and allows the watery vapours, freed from iodine, to be absorbed in weighed drying tubes. When it is merely required to determine relatively small quantities of iodine, the metal spirals do good service; but as the proportion of moisture in iodine is generally small, it is desirable to take for its determination not too small a quantity of the material. Hence the danger that the iodine may escape absorption by the spirals is increased, except they are made of an inconvenient length.

My procedure, in which this risk is not merely obviated, but the apparatus is of the utmost simplicity, is as follows:—

The iodine to be examined is allowed to fall from the weighing-glass into a test-tube of about 1 c.m. in width and 6 c.m. in length; it is at once superstratified with from four to five times its quantity of silver powder, previously ignited; the tube is closed with a glass stopper, ground to fit its mouth, and weighed immediately; or, if in case of a high temperature of the air, the silver is being attacked by the iodine on mutual contact, not until completely cold. The open tube, which may be set in a small beaker, is heated upon an asbestos plate, so gently that only a very slow formation of silver iodide takes place. As this reaction can always be observed, it may be easily regulated in case of need by removing the beaker from the asbestos plate. With experience, which is easily acquired, there is no risk of the escape of even traces of iodine. Should it really occur, it would be inevitably shown by a

change of the colour of the silver powder; the silver powder then appears attacked to its upper layer, whilst if the operation is correctly managed, the upper portions of the silver must remain unchanged. During the formation of silver iodide, the water which escapes is condensed in the colder parts of the tube, from which, after the complete absorption of the iodine, it is expelled by a higher temperature. When this takes place, the tube is stoppered up, allowed to cool, and weighed. The difference shows the quantity of water which has been present in the iodine. The determination, with all the preparations, scarcely requires one hour.

The method allows of an accurate determination of moisture in iodine, even if chlorine and bromine are simultaneously present; it loses, however, its trustworthiness if considerable quantities of cyanogen are present.—*Chemiker Zeitung*.

HAMBURG WATER.

By JOHN B. COPPOCK, F.C.S.,
Analyst to the London Water Co.

THE spread of cholera at Hamburg has been one of the most noticeable points in the present cholera scare.

The connection between cholera and its diffusion in a polluted water medium has been strengthened and developed by many remarkable outbreaks extending over the last thirty years. The ravages of the disease have been shown to be coincident in time and space with the use of water from impure wells, the introduction of a pure and fresh supply bringing about the abatement of the outbreak.

Whether cholera can be produced by animal organic matters not of a specific nature has not yet been proved, but it has been proved that a polluted water supply is a splendid medium for the propagation of the cholera poison; anyhow, the endemic area of cholera approximates very closely to the area supplied with a polluted water.

By the kindness of a friend I have been enabled to get a sample of Hamburg Water taken from the mains by an ordinary tap, just as it is supplied for drinking purposes to the houses. The water gave the following results:—

PHYSICAL EXAMINATION.

Appearance	Turbid, very yellow.
Taste	Slightly unpleasant.
Odour	Extremely small.
Deposit	Small, dirty looking.

MICROSCOPIC EXAMINATION.

Animal and vegetable matters, inorganic particles.

QUANTITATIVE RESULTS (Mean of Two Analyses).

Total solids	81.25 grains per gal.
Chlorine	33.04 "
Free ammonia	0.0746 "
Albumenoid ammonia	0.0205 "
Sulphates	2.37 "
Nitrates	1.95 "
Oxygen (consumed in 15 mins.)	0.065 "
" (consumed in 4 hours)	0.24 "

Cultivation in nutrient gelatin produced the usual crop of bacteria, bacilli, micrococci and fungi, but the consumption of the water has not produced any choleraic symptoms in a cat. The water is very likely not specifically polluted, it producing a lowered state of the system and tendency to diarrhoea, favourable to the specific contagion. As the water is originally taken from the Elbe it may with fairness be described as little short of "dilute sewage." The Senate of Hamburg is going to be asked to authorise the immediate construction of

Artesian wells for the production of a pure water supply, —not too soon to take such steps in the present condition. A better water supply might have saved Hamburg from the present epidemic.

TENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee notes with satisfaction a growing appreciation of the Reports on Chemical Bibliography that have been presented to the Chemical Section of the American Association for the Advancement of Science. The Ninth Annual Report was widely circulated, appearing not only in the *Proceedings of the A. A. S.*, but also in the *CHEMICAL NEWS*, the *J. Anal. Appl. Chem.*, the *J. Am. Chem. Soc.*, and the *Scientific American*.

The Committee congratulates the Section on the fact that these annual reports have in large measure accomplished one of the principal objects sought, viz., that of directing attention to the importance of compiling bibliographies, catalogues, and indexes to the voluminous literature of chemistry. While little systematic work has been undertaken, duplication of labour has been prevented and independent efforts have accomplished much; how much appears in the list of bibliographies forming the Appendix to this Report. Chemists are more and more perceiving the advantages of attaching carefully prepared bibliographies to their monographs; recently this plan has been pursued in the important *Bulletins of the Chemical Division of the United States Department of Agriculture*. Thus a collection of special bibliographies is gradually forming, destined to be of inestimable value to the chemist. The Committee expresses the hope that this collection will grow in the future much faster than in the past, and suggests that members of the Section of Chemistry seriously consider in what way they can individually contribute to the cause.

During the current year the following indexes have been published.

1. A Bibliography of the Electrolytic Assay of Copper. By Stuart Croasdale. In *J. Anal. Appl. Chem.*, v., pp. 133 and 184 (March and April, 1891).
2. An Index to the Literature on the Estimation of Nitrogen by Kjeldahl's Method and its Modifications. By Lyman F. Kebler. In *J. Anal. Appl. Chem.*, v., 260, (May, 1891).
3. An Index to the Literature on the Estimation of Nitrogen by all other Methods. By Lyman F. Kebler. In *J. Anal. Appl. Chem.*, v., 264 (May, 1891).
4. Index to the Literature of the Tannins. By Professor Henry Trimble, Ph.M., of Philadelphia. This forms an Appendix to: "The Tannins; a Monograph on their History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents," by the author named. Philadelphia, 1892. Vol. I., 168 pp., 12mo. The Index occupies pp. 101—165, and the titles are arranged chronologically with an alphabetical index of authors. The whole is admirably printed and obviously exhaustive.
5. Index to the Literature of Angelic and Tiglic Acids, from 1842—91. By Henry P. Talbot, Ph.D. *Technological Quarterly*, vol. v., Nos. 1 and 2 (Massachusetts Institute of Technology, Boston). Contains an historical summary, and author- and subject-indexes.
6. Bibliography of Analytical and Applied Chemistry for the Year 1891. By H. Carrington Bolton. *J. Anal. Appl. Chem.*, vol. vi, p. 61, 1892.

We chronicle also the following contributions to chemical bibliography:—

7. Professor Thomas B. Stillman, in his papers on "Animal, Marine, and Vegetable Oils used in Lubrication," has paid especial attention to the bibliography of the subject, grouping under each division of his essay many references to periodical literature and other (*J. Anal. Appl. Chem.*, v., April, June, and December, 1891).

8. A list of Chemical Synonyms is found in pages 661—675 of the Appendix to: "The Scientific American Cyclopedia of Receipts, Notes, and Queries." Edited by Albert A. Hopkins. New York, 1892. 8vo. Ill.

9. Prof. Samuel P. Sadtler's "Handbook of Industrial Organic Chemistry" (Philadelphia, 1891, pp. xiv.—519. Roy. 8vo. Ill.) contains bibliographies at the close of each chapter embracing the following topics:—

- (1). Petroleum and Mineral Oil Industry.
- (2). Industry of the Fats and Fatty Oils.
- (3). Industry of the Essential Oils and Resins.
- (4). The Cane and Sugar Industry.
- (5). The Industries of Starch and its Alteration Products.
- (6). Fermentation Industries (Malting, Brewing Wines, Spirits, Vinegar, Flour, and Bread).
- (7). Milk Industries.
- (8). Vegetable Textile Fibres and their Industries.
- (9). Textile Fibres of Animal Origin.
- (10). Leather, Glue, and Gelatin.
- (11). Destructive Distillation Industries.
- (12). Artificial Colouring-matters.
- (13). Natural Dye Colours.
- (14). Bleaching, Dyeing, and Textile Printing.

The Bibliographies are chronologically arranged one-line titles.

Professor S. F. Peckham reports substantial progress on his Bibliography of Bitumen; Professor Arthur M. Comey on his Dictionary of Solubilities; and Dr. Alfred Tuckerman on his Bibliography of Mineral Waters. Dr. Arnold Eiloart, of New York, has completed the MS. of an Index to the Literature of Stereochemistry; this will appear as an appendix to his review of the subject in the *Am. Chem. J.* The whole will also be issued independently. Prof. Charles E. Munroe announces Part II. of his Index to the Literature of Explosives, to be published shortly. Dr. H. C. Bolton's Select Bibliography of Chemistry has been accepted by the Smithsonian Institution for its Miscellaneous Collections and is in the hands of printers.

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
ALBERT R. LEEDS,
ALEXIS A. JULIEN,
JOHN W. LANGLEY,
ALBERT B. PRESCOTT,
ALFRED TUCKERMAN.

APPENDIX TO TENTH ANNUAL REPORT OF COMMITTEE ON INDEXING CHEMICAL LITERATURE.

List of Indexes to Chemical Literature.

- Abbreviations of Titles of Chemical Journals.* By H. Carrington Bolton [and others]. *J. Anal. Chem.*, vol. ii., Part 1, Jan., 1888.
- Amalgams; Index to the Literature of.* By Wm. L. Dudley, in his Vice-Presidential Address to the American Association for the Advancement of Science, at Toronto. *Proceedings A. A. S.* for 1889, pp. 161—171, 1890. 8vo.
- Ammonia from Atmospheric Nitrogen*, An Index of Researches upon the Production of. By Ezra J. Ware. Published in *Proc. Michigan State Pharm. Assoc.*, 1888. H. J. Brown, Secretary, Ann Arbor, Mich.
- Analytical Chemistry*, Bibliography of, for the year 1886. By H. Carrington Bolton. *J. Anal. Chem.*, vol. i., pt. 3, July 1887.
- [The same] for 1887. *Idem.*, vol. ii., pt. 1, Jan., 1888.

* From Advance Proofs of the *Proceedings of the American Association for the Advancement of Science*, vol. xli., 1892.

- [The same] for 1888. *Idem.*, vol. iii., pt. 4, Oct., 1889.
- [The same] for 1889. *Idem.*, vol. iv., pt. 1, Jan., 1890.
- [The same] for 1890. *Idem.*, vol. v., No. 3, March, 1891.
- Analytical and Applied Chemistry**, Bibliography of, for the year 1891. By H. Carrington Bolton. *J. Anal. Appl. Chem.*, vol. vi., p. 61, 1892.
- Angelic and Tiglic Acids**, Index to the Literature of. By Henry P. Talbot. *Technological Quarterly*, Boston, vol. v., Nos. 1 and 2, 1892.
- Beeswax and Waxes Used in Adulterating Beeswax**, Bibliography of. By Harvey W. Wiley [Editor]. *Foods and Food Adulterants*. Part vi. *Bulletin* No. 13, Division of Chemistry, U.S. Department of Agriculture, Washington, 1892. 8vo., pp. 886—871.
- Butines and their Halogen Addition Products**, Index to the Literature of the (1863—1888). By Arthur A. Noyes. *Technological Quarterly*, Boston, December, 1888. Published at the Massachusetts Institute Technology.
- Butter**, Bibliography of. By Elwyn Waller. In *Second Annual Report of the N.Y. State Dairy Commissioner*, 1886.
- Chemistry**, a Bibliography of, for the year 1883. By H. Carrington Bolton. In "An Account of the Progress of Chemistry in the Year 1883." *Smithson Report for 1883*. Washington, 1884. 8vo.
- [The same] for 1884, 1885, 1886, in *Smithsonian Reports* for said years.
- Chemistry**, a Bibliography of, for the year 1887. By H. Carrington Bolton. Washington, 1888. "Smithsonian Miscellaneous Collections," No. 665. 13 pp., 8vo.
- Columbium**, Index to the Literature of. 1801—1887. By Frank W. Traphagen. "Smithsonian Miscellaneous Collections," No. 663. Washington, 1888. pp. [iv.], 27, 8vo.
- Copper**, Electrolytic Assay, Bibliography of. By Stuart Croasdale. *J. Anal. Appl. Chem.*, v., 133 and 184. (1891).
- Electrolysis**, Index to the Literature of; 1784—1880. By W. Walter Webb. *Annals of New York Academy of Sciences*, vol. ii., No. 10, 1882. Pp. 44, 8vo.
- N.B.—This has been translated into French by Donato Tommasi, Paris, 1889.
- Explosives**, Index to the Literature of. Part I. By Charles E. Munroe. Baltimore, 1886. Pp. 42, 8vo.
- Part II. in press (1892).
- Food Adulteration and its Detection**, Bibliography of. By Jesse P. Battershall. In "Food Adulteration and its Detection." New York, 1887. 8vo.
- Geometrical Isomerism**, a Bibliography of. Accompanying an Address on this subject to the Chemical Section of the American Association for the Advancement of Science, at Indianapolis, August, 1890. By Robert B. Warder. *Proc. A. A. S.*, vol. xxxix., Salem, 1890, 8vo.
- Heat**, Dictionary of the Action of Heat upon certain Metallic Salts; including an Index to the principal literature upon the subject. Compiled and arranged by J. W. Baird; contributed by A. B. Prescott, New York, 1884, pp. 70, 8vo.
- History of Chemistry**, Outlines of a Bibliography of the. By H. Carrington Bolton. *Ann. Lyc. Nat. Hist.*, vol. x., pp. 352—361. New York, 1873.
- Honey**, Bibliography of. By Harvey W. Wiley [Editor]. "Food and Food Adulterants," Part vi. *Bulletin* No. 13, Division of Chemistry, U.S. Department of Agriculture, Washington, 1892, 8vo., pp. 871—874.
- Iridium**, Bibliography of the Metal. By Nelson W. Perry, in Prof. W. L. Dudley's paper on Iridium, published in "Mineral Resources of the United States," calendar years 1883 and 1884. Washington, 1885, 8vo.
- Light**, Chemical Influence of, a Bibliography of. Alfred Tuckerman. "Smithsonian Miscellaneous Collections," No. 785, Washington, 1891, pp. 22, 8vo.
- Manganese**, Index to the Literature of; 1596—1874. By H. Carrington Bolton. *Annals of the Lyceum of Natural History*, New York, vol. xi., November, 1875, pp. 44, 8vo.
- Milk**, Bibliography of. By Edward W. Martin. In *Second Annual Report of the N. Y. State Dairy Commissioner*, 1886.
- Nitrogen**, Estimation of. By Kjeldahl's Method, Index to the Literature. By Lyman F. Kebler. *J. Anal. Appl. Chem.*, v., 260 (1891).
- Nitrogen**, Fixation of Atmospheric. For bibliographical data see *Historical Summary* on this subject by A. A. Breneman in *J. Am. Chem. Soc.*, xi. (1889).
- Ozone**, Index to the Literature of; 1875—1879. By Albert R. Leeds. "Annals of the New York Academy of Sciences," vol. i., No. 12, 1880, pp. 32, 8vo.
- Ozone**, Index to the Literature of, 1879—1883; accompanied by an Historical Critical Résumé of the Progress of Discovery since 1879. By Albert R. Leeds. *Annals N. Y. Academy of Sciences*, vol. iii., p. 137, 1884. 16 pp., 8vo.
- Periodicals**, A Catalogue of Chemical. By H. Carrington Bolton. *Annals N. Y. Acad. Sci.*, vol. iii., pp. 159—216. New York, 1885. 8vo. Also: *CHEMICAL NEWS* Print, London, 1886. 12mo.
- Supplement to (the same). *Ann. N. Y. Acad. Sci.*, vol. iv., Feb., 1887. 4 pp., 8vo.
- Periodicals**, Short Titles of, current in 1887. By H. Carrington Bolton. *J. Anal. Chem.*, vol. i, Part 1, 1887. 4 pp., 8vo.
- Peroxide of Hydrogen**, Index to the Literature of; 1818 to 1878. By Albert R. Leeds. *Annals N. Y. Acad. Sci.*, vol. i., No. 13, 1880. 11 pp., 8vo.
- Peroxide of Hydrogen**, Index to the Literature of; 1879 to 1883. By Albert R. Leeds. *Annals N. Y. Acad. Sci.*, vol. iii., p. 153, 1884. 3 pp., 8vo.
- Petroleum**, A Bibliography of. By Prof. S. F. Peckham. Report on the Production, Technology, and Uses of Petroleum and its Products. Report of the Census of the United States. Vol. x., 1884. 4to, pp. 281—301.
- Ptomaines**, A Bibliography of; accompanies Victor C. Vaughan's *Ptomaines and Leucomaines*, Philadelphia, 1888, pp. 296—314, 8vo.
- Speed of Chemical Reactions**, Literature of. By Robert B. Warder. *Proc. Amer. Assoc. Adv. Sci.*, vol. xxxii., 1883. 3 pp., 8vo.
- Specific Gravity of Solids and Liquids**, A Table of. The Constants of Nature, Part 1 (new edition, revised and enlarged). By Frank Wigglesworth Clarke. Washington, 1888. *Smithsonian Miscellaneous Collections*, No. 659, pp. 11—409, 8vo.
- Spectroscope**, Index to the Literature of. By Alfred Tuckerman. *Smithsonian Miscellaneous Collections*, No. 658. Washington, 1888, pp. 10—423, 8vo.
- Starch Sugar**, Bibliography of. By Edw. J. Hallock. Appendix E to Report on Glucose prepared

- by the National Academy of Sciences, in response to a request made by the Commissioner of Internal Revenue. U. S. Internal Revenue, Washington, D. C., 1884. 44 pp. 8vo.
- Tannins*, Index to the Literature of. By Henry Trimble. The Tannins. Philadelphia, 1892. Vol. i., Appendix.
- Tea, Coffee, and Cocoa Preparations*, Bibliography of the Literature on. By Guilford L. Spencer. Food and Food Adulterants. Part vii., Appendix A. *Bulletin* No. 13, Division of Chemistry, U. S. Department of Agriculture. Washington, 1892. 8vo., pp. 991-1009.
- Thermodynamics*, Index to the Literature of. By Alfred Tuckerman. Smithsonian Miscellaneous Collections, No. 741. Washington, 1890. pp. 6-329. 8vo.
- Titanium*, Index to the Literature of; 1783-1876. By Edw. J. Hallock. *Annals of the New York Academy of Sciences*. Vol. 1, Nos. 2 and 3, 1877. 22 pp., 8vo.
- Uranium*, Index to the Literature of. By H. Carrington Bolton. *Annals of the New York Lyceum of Natural History*, Vol. ix., February, 1870. 15 pp. 8vo.
- Uranium*, an Index to the Literature of; 1789-1885. By H. Carrington Bolton. Smithsonian Report for 1885. Washington, 1885. 36 pp., 8vo.
- Vanadium*, Index to the Literature of. By G. Jewett Rockwell. *Annals of the New York Academy of Sciences*, Vol. i., No. 5, 1877. 32 pp., 8vo.

A PROCESS FOR THE REMOVAL OF THE LINT FROM COTTON-SEED.*

By WM. L. DUDLEY.

THE "sea-island" or "long-staple" cotton (*Gossypium Barbadosense*) and the Egyptian cotton have naked seed, while the "upland" or "short-staple" cotton (*G. Herbaceum*) of the United States has seed encased in a mass of fibre firmly adherent to the seed-coat.

The seed crushed in England for the extraction of the oil is largely the Egyptian, but in the United States the great source of the oil is the "upland" seed, as the "sea-island" cotton grows over a very limited area. In consequence of this hairy envelope which surrounds the American cotton-seed, decortication is necessary previous to the expression of the oil. The Egyptian and "sea-island" seed need only be crushed, heated, and pressed.

Besides the expense of decorticating the American seed, much "meat" is lost by becoming entangled in the hulls and failing to separate; on this account the oil-yield is lower by several gallons per ton than that from the naked seed, and the yield of "cake" is less as it contains no hulls. The American seed will not stand storage nor shipment well (especially export), as moisture absorbed by the fibrous envelope will enable fermentation to set in.

The process for the treatment of American seed is briefly as follows:—They are (1) run through "linters," which remove as much as possible the cotton which has been left on the seed by the gin; (2) decorticated by a machine which cuts the seed-coat, whereupon the "meat" and the "hulls" fall apart; (3) separated by passing through an inclined revolving screen having meshes which allow the "meat" to fall through, while the "hulls" are retained and roll out at the lower end; or by means of an air blast; (4) the "meat" is heated and

pressed. The hulls are burned, and the ash, rich in potash, has a market value.

All mechanical methods which have been devised to strip the seed of its fibre have proved unsuccessful, either from imperfect performance or lack of speed.

The chemical process described below was devised some time since (U.S. Pat. 344,951) by the author and N. W. Perry, E.M. It has never been tried commercially, but its success is perfect on a small scale.

The seed after linting are subjected to the action of N_2O_3 and SO_2 , either in the above order or mixed together, enough air attending them to "regenerate" the NO . This is probably best accomplished by having the seed descend a chute slowly through which a current of N_2O_3 is ascending, and then into a chute where SO_2 and air are ascending; or they may descend through a chute having an ascending current of N_2O_3 , SO_2 , and air. After a few seconds' exposure to these gases under proper conditions, the fibre on the seed has changed very little in appearance, but its structure is so completely destroyed that the slightest friction causes it to fall into an impalpable powder. The seed are left perfectly smooth, showing no signs of corrosion. They have a slight acid reaction on the outside, but the acid is speedily removed by washing. The seed-coat is very hard, and is impervious to the gases. No trace of acid has ever been discovered in the interior. The seed germinate very quickly if planted. The acidity may also be removed by blowing lime-dust on the seed as soon as they come from the "cleaner" which removes the disintegrated fibre; or they may be carried by a conveyer through lime-water and then through a dryer. The seed are now ready to be crushed and pressed, or they may be shipped and stored as well as Egyptian or "sea-island" seed.

The "cleaner" referred to above may be any good grain cleaner. The disintegrated fibre is quite dry, and is easily converted into glucose.

The N_2O_3 and SO_2 may be generated by any of the well-known processes, but the ordinary methods employed in sulphuric acid making are the most economical. In fact this process should be operated, possibly, in connection with such works; the gases escaping from the cotton-seed chute being absorbed in the tower or conveyed into the leaden chamber, so that there is no loss.

NOTICES OF BOOKS.

Photography Annual. A Compendium of Information upon Photographic Matters and the Annals of Photography for the Past Year, 1892. By HENRY STURNEY. London: Iliffe and Son, 3, St. Bride Street, Ludgate Circus, E.C.

THIS goodly volume opens with a collection of tables, &c., useful to the photographer, though not to him alone.

We notice a table of poisons with characteristic symptoms and antidotes. We presume the author has purposely mentioned those only which the photographer is liable to encounter in his *atelier*. We may here repeat a caution which we have given elsewhere, that no food or drink should be partaken of in laboratories, dye, print, or colour works, or in other localities where chemical operations are carried on.

The list of impurities liable to be present in chemicals will be very useful, especially to the beginner who has not got into the habit of suspecting possible impurities everywhere until he has proved their absence.

We cannot help applauding the remark that "an east wind means bad light, however otherwise bright the day may seem to appear."

The advances made in various sciences by means of photography are chiefly in the direction of astronomy. Chemistry and biology seem to be reaping little direct advantage. Nevertheless, the photo-micro apparatus

* *Journal of Analytical and Applied Chemistry*, Vol. vi., No. 3.

here shown and described (Nos. 109 and 110) will be of great value to the student and the "researcher,"—if we may venture upon this ugly word.

Considering the thoroughly technical character of most of the subject-matter, the typographical accuracy of the work deserves commendation. We notice one error, where "Coleoptera" is transformed into "Coloptera."

The list of the photographic societies of the United Kingdom is wonderful in its extent. Here we are led to a question; we believe and hope that the scientific applications of photography are as yet only in their infancy, and that developments are here in store which are yet quite unexpected. But will the rage for photography as a mere amusement prove permanent? In all human probability not. The professional photographers, the art students, and the men of science to whom the camera with its accessories rank with the microscope, the spectroscope, and the balance will scarcely suffice to keep in action the legion of makers and sellers of apparatus and the really respectable number of journals devoted to the subject.

A Pocket-Book for Miners and Metallurgists. Comprising Rules, Formulæ, Tables, and Notes, for use in Field and Office Work. Compiled by FREDERICK DANVERS POWER, F.G.S. London: Crosby Lockwood and Son, 1892. 12mo, pp. 334.

THIS is one of those thoroughly practical works with which Messrs. Crosby Lockwood and Son are enriching our technological literature. Almost the only error which we can detect is in the table of atomic weights; platinum is given = 196.7, i.e., higher than gold, whilst according to the latest and most accurate determinations it is only 195.

We regret to find Baumé's table for the specific gravities of liquids inserted. It has the twofold defects of being not reducible to direct specific gravity by any simple calculation, and of existing in three discordant modifications. For what purpose it is retained in France and America we are unable to say. A few typographical errors in a work of such technical character can scarcely be avoided. In the section on toxicology we find "dantrin" for "daturine."

The table for calculating the results of chemical analyses strikes us as being much less convenient than that of Rose. The index is very good and the glossary will prove widely useful, since in these days a specialist is often puzzled if he encounters some term belonging to a different speciality. We trust this work will be as widely appreciated as most of its predecessors have been.

The Extra Pharmacopœia. By W. MARTINDALE, F.C.S. Medical References and a Therapeutic Index of Diseases and Symptoms. By W. WYNN WESTCOTT, M.B. Seventh Edition. London: H. K. Lewis, 1892.

MEDICAL science knows no finality. If there are certain diseases which still set the physician at defiance it must be admitted that, as shown by the little volume before us, the latter is constantly adding to and modifying his armoury.

Turning over the leaves we find mention of the double gold and sodium chloride used as an antidote to cobra-poison. But with what success? It must cheer the heart of Bishop Berkeley, if he still studies medical literature, to find that tar and its preparations are again coming more to the front.

A Russian remedy for dropsy which must appal the fair sex consists simply of powdered cockroaches, the "black beetles" of kitchen entomology. As there are a few of these insects in London, it might be well if some enterprising quack would bring them into vogue as a medicine. In sober sadness it is folly to assume that we have yet exhausted nature's resources for the relief and the prevention of disease. Our duty plainly is to go on trying

"all sorts of things" with due scientific precaution until the black list of "opprobria medicinæ" is effaced. The busy practitioner will find the work of Messrs. Martindale and W. W. Westcott exceedingly suggestive.

Catalogue of Standard Second-Hand and New Books, English and Foreign, on Chemistry and the Allied Sciences. Offered by WILLIAM F. CLAY. Edinburgh: University Book Warehouse, 18, Teviot Place.

THIS issue of Mr. W. F. Clay's catalogue presents as a most striking feature complete sets of standard journals, transactions, &c., scarce and often very difficult to obtain, yet offered at exceptionally moderate prices. We may mention as instances a complete set of the reports of the British Association from the commencement in 1845 to 1888; the CHEMICAL NEWS from its commencement in 1860 to the end of last year; the *Journal of the Chemical Society* in fifty-eight volumes, from 1848 to 1890; the *Journal of the Society of Chemical Industry* complete, from the beginning; the *Philosophical Magazine* in 196 volumes, from 1798 to 1890, besides a multitude of rare and valuable chemical and physical works.

The librarians of universities, &c., as well as private collectors of works in any particular department of Science, will find this catalogue an excellent guide to the completion of their sets and the acquisition of desiderata.

The Principal Starches Used as Food. Illustrated by Photo-micrography, with a short Description of their Origin and Character. By W. GRIFFITHS. 62 pp., 25 Photomicrographs. Cirencester: Bailey and Son.

THE object of the author in the publication of this little work is to aid analysts in the identification of such starches as may be met with in the course of their investigations. Starch is so much in use for purposes of substitution or adulteration, that any means by which its fraudulent use can be detected must prove of the greatest utility.

The microphotographs are carefully executed from verified specimens, in most instances prepared by the author himself. They are all photographed under the same magnifying power ($\times 160$), which will aid comparison with other specimens. A short description is given of each starch represented.

One of the most interesting starches, both from its large size and the distinctness of its structural details, is that from the fruit of the potato (*Solanum tuberosum*),—a Jupiter among starches. It is somewhat remarkable that no trace of starch has up to the present time been discovered in the fruit of a closely allied plant, the tomato. This starch, as the author remarks, would be the most suitable on which to carry out investigations relating to its physical structure. The nature of the beautiful concentric markings is still unknown. The chemistry of starch being so fully treated elsewhere is but little mentioned in the present book, and as it is not possible by chemical means to discriminate between the starch of one plant and that of another, the omission is of little moment.

For these determinations the microscope is the only reliable guide; and to the analyst whose work leads him to researches on the admixture of cheaper starches with the more costly, as well as to their use in adulterating other substances, the book and its illustrations must prove of the greatest value.

Everybody's Pocket Cyclopædia of Things worth Knowing. By DON LEMON. London: Saxon and Co.

THE success of the previous editions of this useful reference book has justified the compiler in making many additions to this, the tenth. The pocket-book is almost double the size that it was when first published four years ago, and during that time about 500,000 copies have been

sold. There are, however, still a few alterations which might with advantage be made; for instance, the tables on pages 58, 96, and 97 cannot be properly read without turning the book upside down, but this could easily be rectified. Further, the bulk of page 84 might be omitted, it being merely an old arithmetical puzzle of "how to tell a young lady's age."

These are but minor defects in the book, and do not detract from its value in many other points. It is furnished with an excellent index and is very clearly printed.

The Threshold of Science. By Dr. C. R. ALDER WRIGHT. Second Edition. London: Charles Griffin and Co.

THE number of elementary works of this class published of late years shows that the demand for them is always increasing. Being written with the object of providing a kind of "playbook," which will amuse and at the same time instruct, the "Threshold of Science" is well adapted as a book for boys, giving, as it does, a good insight into the various branches of chemical and physical science, and stimulating a desire for further knowledge. System is becoming so intimately associated with modern everyday life and work that our children cannot too early be given that thirst for knowledge which will so materially assist them in later years.

Constable's Oriental Miscellany. Vol. II. *Popular Readings in Science.* By JOHN GALL, M.A., LL.B., and DAVID ROBERTSON, M.A., LL.B., B.Sc. London: Archibald Constable and Co.

THE authors of this work are certainly to be congratulated upon the very great amount of interesting matter comprised within its limits; we may say that there is scarcely a dull page in the whole volume. It consists, as its title would indicate, of various articles treating of and discussing different modern theories in chemical and allied branches of science; a large part of the book deals with evolution, not only in living bodies and plants, but even going so far back as to apply modern theories to the formation of matter itself, and its subsequent "contraction"—if we may use the term—into elements, suns, planets, &c.

One cannot help being struck by the manner in which these theories seem to spring from Darwinism, as well as the way in which they fit in one with another. The authors lay no claim to originality, but have embodied in their articles the best accepted theories and speculations of recent times. A feature of this book which must not be overlooked is the supply of about half a dozen catalogue slips; there is, however, in this, room for improvement, as these slips, being all the same, give prominence to the name of one of the authors only, while there is no slip whatever with the name of the book itself coming first.

CORRESPONDENCE.

STILLS AND THE EXCISE.

To the Editor of the Chemical News.

SIR,—It may be of interest to your readers to know that the following letter has been received from the Excise Authorities in reply to a memorandum laid before them by Mr. Carteighe (Vice President), in accordance with the request of the Council of the Institute of Chemistry. —I am, &c.,

G. H. ROBERTSON, Secretary.

The Institute of Chemistry,
9, Adelphi Terrace, Strand, W.C.
Sept. 10, 1892.

Inland Revenue, Somerset House,
London, W.C.

SIR,—Having laid before the Board of Inland Revenue your letter of 28th July, I am directed in reply to acquaint you, for the information of the Council of the Institute of Chemistry, that the Board have no desire to extend the obligation to take out a licence to analytical chemists using stills solely for purposes of distilling water. If an analytical chemist called upon to take out a licence by one of the Board's officers will submit his case to the Board they will be prepared to give the matter careful consideration.—I am, Sir, your obedient Servant,

(Signed) W. B. HEBERDEN,
Asst. Secretary.

To M. Carteighe, Esq.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 6, August 8, 1892.

Application of the Measurement of Densities to the Determination of the Atomic Weight of Oxygen.—A. Leduc.—The author gives the molecular weight of the vapour of water as 17.88. Its theoretical density, taking that of hydrogen as a point of departure, would be 0.6212. But it is preferable to set out from the density of oxygen, the compressibility of which is scarcely superior to that of air. We thus arrive at 0.6221. We see that the experimental density of the vapour of water cannot descend below 0.622.

The General Form of the Curves of Ebullition of Compounds with Central Substitution.—G. Hinrichs.—A very mathematical paper, which requires the reproduction of the very complicated diagram.

Existence in Soils of an Acid Mineral Substance not yet Determined.—Paul de Mondesir.—The substance which the author points out is very stable. It is not destroyed on the complete combustion of the organic matter at dull redness, even when deprived of its bases by previously washing the soil with dilute acids. It resists to a great extent hot, concentrated hydrochloric acid, which dissolves all the iron that gives a red colour to burnt soils and likewise nitric acid boiling for some hours. It is preserved almost entirely in soil submitted to ebullition for two or three minutes in a solution of caustic potassa containing about 15 per cent of aq. potassa. The author has not yet been able to determine its composition. It is probably a silicate of a clayey character.

Calcareous Soap and the Explosions of Steam-Boilers.—A. Vivien.—The author does not consider the formation of this lime-soap proved. The crock formed in the boilers is not found to contain fats or fatty bodies, and the alleged lime-soaps contained only from 0.160 to 0.000 of fatty matter.

On Pupine, a New Animal Substance.—Dr. A. B. Griffiths.—Pupine is extracted from the integuments of lepidopterous pupae. Its mean composition is $C_{14}H_{26}N_2O_5$. It is colourless and amorphous. It dissolves in mineral acids, being converted into leucine and carbonic acid. It is not dissolved by neutral solvents.

Colouring-Matter of Micrococcus Prodigiosus.—Dr. A. B. Griffiths.—The mean composition of this pigment is $C_{38}H_{56}NO_5$. The alcoholic solution shows with the spectroscope two absorption-bands, one in the blue and the other in the green. Acids turn it to a carmine and alkalis render it yellowish. This parasite

may be completely destroyed by syringing the crops with a solution of ferrous sulphate.

Vol. cxv., No. 7, August 16, 1892.

Certain New Compounds of Piperidine.—Raoul Pictet. — Piperidine, a secondary base, yields with salts of silver compounds much more stable than those resulting from the union of pyridine, a tertiary base, with the same salts. In pyridine the facility of combination with salts of silver increases from the chloride to the bromide and the iodide. In piperidine the inverse order prevails. Silver chloride fixes 2 mols. $C_5H_{11}N$; the combination of this salt with C_5H_5N is not stable at the ordinary temperature. Silver bromide and cyanide fix 2 mols. $C_5H_{11}N$ and only 1 mol. C_5H_5N . Silver iodide fixes only 1 mol. of each of these bases.

Application of Chemical Analysis to Fix the Age of Præhistoric Human Bones.—Ad. Carnot. — The author draws conclusions from the comparative proportion of fluorine, which is found to be larger the older the bones.

— — —
Zeitschrift für Analytische Chemie.
Vol. xxx., Part 6.

(This issue has appeared only after the two first parts of Vol. xxxi.).

Determination of Oil of Mustard.—Dr. A. Schlicht. — This paper will be inserted at length.

The Question of the Fermentability of Dextrines.—L. Medicus and C. Immerheiser. — The authors decide that the dextrines of crude potato-sugar are capable of fermentation if a sufficient quantity of "press yeast" is applied, though it resists beer yeast.

Different Solubilities of Strontium and Calcium Chromates in dilute Alcohol, and on the Possibility of Separating these Two Alkaline Earths as Chromates.—W. Fresenius and F. Ruppert. — A useful qualitative separation can be founded upon the differences recognised if the quantities of strontium are not too small, but it does not suffice for a quantitative separation.

Determination of the Specific Gravity of Sparingly Fluid Substances.—J. W. Bruehl. — Already inserted.

Apparatus for Determining Refractive Power.—J. Bernström (German patent). — This apparatus is identical with Soudén's liquescope.

Air Thermometer for Technical Purposes.—A. H. Sabine. — (From the *Journal of the American Chemical Society*).

Apparatus for Determining the Temperature of Explosions.—S. Bein. — Already inserted.

Agitation Apparatus for Electrolytic Operations.—N. von Klobulow. — (From the *Journal für Praktische Chemie*).

Development of Gases.—E. Dossaert (*Chem. Zeit.*). — A sulphuretted hydrogen apparatus. Similar in principle is the gas generator of W. Oakes Kibble described and figured in the *CHEMICAL NEWS*. A gas apparatus which may be extemporised in any laboratory is that proposed by Eustace Thomson in the *CHEMICAL NEWS*. Other apparatus for generating gases have been proposed by Grünwald (*Chemiker Zeitung*), Raikow (*ibidem*), and Habermann (*Naturf. Verein in Brünn*).

Hydrogen Sulphide free from Arsenic.—M. Habermann. — Already inserted.

Preparation of Pure Hydrogen.—M. Berthelot. — (From the *Bull. Soc. Chim. Paris*).

Development of Gases.—W. H. Hillyer (*Amer. Chem. Jour.*) and Pollak and Wilde (*Chemiker Zeitung*) have drawn attention to the proposal of letting the acids fall drop by drop upon a sufficiently deep stratum of the solid ingredient, so that the acid is thoroughly utilised before it flows away.

Production of Oxygen.—J. Volhard (*Liebigs Ann.*), employs the mutual reaction of hydrogen and chloride of lime.

Production of Oxygen.—G. Kassner (*Chem. Zeitung*), employs the reaction of potassium ferricyanide with hydrogen peroxide in presence of alkali.

Development of Gases.—M. Neumann (*Journ. für Prakt. Chemie*). — Already inserted.

Hydriodic Acid.—E. Etard (*Bull. Soc. Chim. Paris*), obtains a continuous current without disconnecting the apparatus by means of a flask with a lateral tubulure, through which passes the gas delivery tube.

Some New Small Laboratory Appliances.—S. Schiff (*Chemiker Zeitung*), and Fr. Stolba (*Berichte der boehm. Gesell. der Wissenschaft*). — Both devices are figured and described here.

A Closure for Burettes without a Cock.—M. Dannbacher (*Pharm. Central Halle*). — Already inserted.

New Stopper for Reagent-Bottles.—A. Gawalowski. — Already inserted.

Ground Joints and Glass Cocks for Vacuum Apparatus.—W. A. Shenstone. — (From the *Journal of the Chemical Society*).

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APPOINTMENT OF DEMONSTRATOR IN CHEMICAL DEPARTMENT.

The Council invite applications on or before the 24th September, 1892, for the above appointment. The selected candidate will be required to enter upon his duties immediately. Particulars of the stipend, conditions, and duties will be sent on application to the Secretary, Mr. G. H. MORLEY, Mason College, Birmingham, to whom all applications for the appointment should be sent.

G. J. JOHNSON,
President of the Council

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1713.

ON THE COMPOSITION OF SEA-WATER.

By DR. F. GIBSON.

It is not possible to obtain a really accurate direct determination of the total salts contained in sea-water, as, during the course of evaporation, however carefully conducted, indeterminate quantities of carbonic acid from the bicarbonates are given off, owing to the fact that magnesium chloride decomposes. For the purposes of comparison and hydrographical record, the relative proportion of total salts in different sea-waters is most generally, and also most accurately, derived from a determination of the density of the sea-waters in question. Dittmar came to the conclusion, from an elaborate examination of sea-water collected during the *Challenger* expedition, that different samples of sea-water differed from one another, in so far as any rate as the saline constituents were concerned, simply by the amount of water which they contained,—that is to say, they might be more or less diluted, but the relative proportions of the saline constituents to one another was constant. If this could be laid down as a practically general rule it is obvious that, instead of a determination of density, one might rely equally upon the determination of one of the principal saline constituents. It would be simply a question as to which method was at once the most accurate and most easy.

This is not, however, an altogether easy matter to decide, and authorities differ, some considering determinations of the chlorine more accurate and others a determination of the density. The fact is that, if a high degree of accuracy is necessary, both are difficult. For the purposes of a mere comparison of salinities, it appears to me that there can be little doubt that preference should be given to density determinations by means of hydrometers such as have been used so successfully by Mr. J. Y. Buchanan. It is, however, very obvious that the relative proportions of the salts in sea-water must be altered more or less, when sea-water is mixed with water draining from the land. The amount of alteration will depend not merely upon the quantity of land-water mixed with the sea-water, but also upon the nature of the land-water itself. Thus the water pouring into the Moray Firth from the Rivers Spey and Findhorn makes a scarcely appreciable difference in the relative proportions of the saline constituents, because these waters are exceptionally pure. On the other hand, the river-water flowing into the Baltic has a very appreciable effect upon the chemical composition of the saline constituents, so that by determining accurately the composition of a Baltic water and Moray Firth water, of the same density, we should find a very appreciable difference between the two. We should find, for instance, the percentage of chlorine lowered as the percentage of sulphuric acid increased in the Baltic water. A still more marked difference will be found in the proportion of carbonates, which would be much greater in the Baltic water. It will be observed that this question of the difference of composition of the saline constituents must be clearly distinguished from any question of mere alteration in density or salinity, and would remain altogether undetected if either of the two methods referred to above were applied singly to such waters. Any mere determination of the density or of the chlorine, considered separately, would throw no light whatsoever upon this question; but if sufficiently accurate determinations of both the percentage of chlorine and density were taken, the difference would become at once manifest.

Dittmar, in formulating his proposition that the relative proportion of the saline constituents of true ocean-water is practically constant, made use of the following formula:—

$$\frac{S - W}{4t \quad 4t} = D$$

X

In this formula X is the weight of chlorine in a thousand parts of the sea-water, or, more correctly, the total halogen (chlorine, bromine, and iodine) calculated as chlorine.

S, signifies specific gravity of sea-water; W, specific gravity of distilled water; the subscript numeral to the left of the letters indicates the temperature at which a volume of distilled water is considered to represent unit weight; the subscript *t* to the right of the letters indicates the temperature at which the respective specific gravities are taken.

The value of the above ratio is, according to Dittmar, constant. As the salts derived from the drainage of land contain relatively large proportions of carbonates and sulphates along with a relatively very small proportion of chlorides, it is obvious that the value of the above ratio must be altered when sea-water is mixed with land-water. Dittmar determined the value for this ratio, and found it equal to 1.4600. In 1883 this ratio was determined for a number of samples collected from different parts of the Moray Firth, and of widely varying density. Some were collected far out to sea; others were collected near the mouths of rivers and far up the Inverness Firth; these samples of course having very low density or salinity. The value for the above ratio, however, in all the different samples approximated closely to the value found by Dittmar. The meaning of this is simply that the ratio of the saline constituents to one another had not been altered, and the explanation of this somewhat unexpected result is to be found in the great purity of the land-water flowing into the Moray Firth. Certain samples collected in the Baltic in 1886 gave very different results. In these samples the salinity or density decreased, of course, as the distance from the sea increased; that is to say, the further from the sea and the further into the Baltic, the lower the density of the water, which should be mixed with a large proportion of the land-water flowing into the Baltic. The value of the above ratio, or, for the sake of brevity, the value for "D," increased as the density or salinity increased.

Now this change in the value for "D" indicates simply a change in the ratio of the salts of the saline constituents to one another, according to the proportion in which the sea-water was diluted by the land-water of different saline composition flowing into the Baltic. The percentage of chlorine diminished because the percentage of chlorine in the saline constituents of the river-waters is very much smaller than in the saline constituents of sea-water proper. Thus an increase in the value for "D" results from admixture of sea-water with the land-water, whenever the land-water contains an appreciable quantity of salts, as the saline constituents of land-water contain invariably a small proportion of chlorine; but such brackish water will also be characterised in a second manner, and to this I wish to call special attention, because, as will be seen later on, an alteration in the value of "D" does not necessarily indicate admixture of sea-water with land-water.

The saline constituents of river-water contain a relatively large proportion of carbonates; that is to say, constituents capable of neutralising hydrochloric acid. If we take "A" as representing the weight in grammes of carbonic acid equivalent to the hydrochloric acid required to neutralise 1000 parts of sea-water, or what is usually known as the alkalinity, and substitute "A" for "X" in the above ratio, we should, in the case of ocean-water proper, on Dittmar's supposition, have constant

value from this ratio also, which we may call "D A"; but in the cases of such samples of brackish water as were collected in the Baltic it will invariably be found that the value for "D A" decreases as the value for "D" increases; that is to say, the alkalinity, or, in other words, the proportion of carbonates in such waters, increases as the proportion of chlorine decreases, so that ocean-water when mixed with land-water will show an increased value over "D," signifying a lower percentage of chlorine in the total salts, and an increased value for "D A" signifying an increase in the proportion of carbonates in the total salts.

It will be remembered that the samples collected in the Moray Firth in 1883, although of greatly varying density, many of them being largely mixed with land-water, all gave a ratio for "D" approximating closely to Dittmar's value for ocean-water. In 1886 a second batch of samples was collected from the Moray Firth. As before, they varied greatly in density, according to the position in which they were taken; that is, according as they were more or less diluted with river-water. The value of "D" was found nearly constant in all these samples, but was altogether different from that obtained previously. Remembering the great purity of the waters flowing into the Moray Firth, the difference in the chemical composition of the saline constituents implied by this new value for "D" seemed almost unaccountable, and it was natural to suspect some flaw in the methods of observation. Fortunately the density and the chlorine of some samples of water collected in 1883 had been determined. As these determinations were made with the same instruments, the same standard solutions, and at the same time as the determinations of the second batch of samples, and as the determinations were moreover all completed before any of the results were calculated, it was obvious that, if this change in the value of "D" were in any sense due to the method of working, this would have its effect upon the results obtained with these samples. Now these samples collected in 1883 all gave practically the same value for "D" as they had done before when first analysed. This in fact constituted a cross test of the most stringent character. There was therefore no escape from the conclusion that the two different values for "D" corresponded to two distinct kinds of sea-water, because, as will be observed, the increase in the value of "D" cannot be accounted for by admixture with the extremely pure waters flowing into the Moray Firth.

During subsequent cruises of H.M.S. *Fackal*, in the North Sea, evidence was in point of fact obtained that there are two kinds of sea-water in the North Sea.

Had we nothing to guide us but determinations of the value of "D" it might, by a great stretch of imagination, be supposed that these remarkable differences in the value for "D" were due to admixture of ocean water proper with such water as flows into the Baltic, though it would be necessary to suppose that these waters had become concentrated by evaporation to about one fourth of their original bulk, because it was not until the salinity of the samples collected in the Baltic had decreased to about one-fourth of the salinity of normal sea-water, such as is found in the middle of the North Sea, that the value for "D" had increased so much as to become equal to the value for "D" in this second batch of Moray Firth samples. But this idea is entirely negated by the fact that, although the value for "D" was greatly increased in these samples, the value for "D A" remained practically constant. It is impossible to reconcile this with the supposition that the alteration in the value of "D" is simply due to admixture with land-water. To sum up:—

The value for "D" in thirteen 1883 samples varied within the limits of 1.4595 and 1.4551. The value for "D" in the forty-five samples collected in 1886 varied within the narrow limits of 1.4675 and 1.4735, and only four samples gave a value lower than 1.4700.

Off the north coast of Scotland, in Jan., 1889, twelve samples varied within 1.4576 and 1.4555.

Seven samples from high northern latitudes (between 62° and 79° N. lat.), in summer, 1888, varied from 1.4726 to 1.4704.

The only cause which seems to the author sufficient to account for these differences is admixture with water derived from the melting of Arctic water ice. According to Pettersson's observations the water obtained by melting sea-water ice from Arctic regions, and also from the Baltic, contains a much higher proportion of sulphates to chlorides than that characterising the sea-water from which the ice was produced; that is to say, the value for D is greater in the water obtained by melting sea water ice than in sea-water in which the ice originally formed.

There seems good reason to hope that by further investigation along the lines suggested in this brief abstract, it will be possible to trace to their origin the waters carried by different oceanic currents, and thereby to throw much light upon some of the most difficult and most important of oceanographic problems.

ON THE DISSOCIATION OF ELECTROLYTES IN SOLUTION AS SHOWN BY COLORIMETRIC DETERMINATIONS.

By H. M. VERNON, B.A.

(Concluded from p. 144).

The Relations of the Colours of Salts to One Another.

In addition to determining the changes of colour of salt solutions on dilution and on rise of temperature, the colours of the solutions of the different salts were compared against each other wherever possible. The normal solutions were generally compared. From the values so obtained, and from the values for the decrease of colour of the salts on dilution, the colour ratios at other dilutions can easily be calculated. In several cases the solutions were compared with each other at two dilutions as a test of the correctness of the colour comparisons. The experimental numbers agreed well with the calculated.

Base.	Colouration for—			
	Chloride.	Sulphate.	Nitrate.	Acetate.
Cupric.. ..	100	96.9	110.7	877.7
Nickel.. ..	100	87.8	81.1	—
Cobalt.. ..	100	78.1	71.8	—
Uranyl.. ..	100	142.2	68.4	51.0
Chromic.. ..	100	79.9	—	—
Ferric.. ..	100	—	—	2147.0

In most cases the other salts were compared directly with the chloride, but in the case of copper they were compared with the sulphate. Of cupric salts the normal solutions were compared, except in the case of the acetate when the 2.5 litre solution was used. The solution of this salt, it will be observed, is nearly eight times darker in colour than that of any other cupric salt. As has been shown, it also dissociates more on dilution than any other cupric salt. The probable reason of this is that copper acetate in its concentrated solutions is not dissociated to nearly so great an extent as any of the other salts, and therefore forms solutions of much darker colour, and also dissociates more on dilution. Thus Kohlrausch has shown (*Pogg. Ann.*, ciii., p. 35), that most sulphates, nitrates, and chlorides are more than half dissociated even in their normal solutions, whilst acetates are only slightly dissociated. Cupric nitrate solution shows the next greatest colour effect. The colour effect of copper chlorate solution was 85.2. The colour of the normal solution of the chloride was too greenish for accurate

comparison, so the decinormal solution, which had just the same tint as the other solutions, was compared, and the value for the normal solution calculated from this. With the exception of the chloride the solutions of all the cupric salts appeared to be of exactly the same shade of colour. The colour effect of the decinormal solution of the chlorate was found to be 83.6, the calculated value being 82.8.

Of nickel salts the chloride shows the greatest colour effect, then the sulphate, and then the nitrate. Solutions of the chloride were very slightly more yellowish in tinge than those of either the sulphate or nitrate. Cobalt salts show the same general relations to each other as nickel salts. The tint of the solution of the chloride was slightly more purple than that of the sulphate or nitrate. The decinormal cobalt nitrate solution was found to have the colour value 82.4, the calculated being 82.8. The uranium salt solutions compared were of 2.5 litre strength, and not normal. The value for the acetate is rather remarkable, as instead of being greater than those of the other salts, like copper acetate, it is much smaller than any of them. The value found for decinormal uranyl sulphate was 145.4, the calculated being 148.0. Of chromium salts only the sulphate and chloride could be compared, the alum being violet in colour and the nitrate brown. Only the decinormal solutions of these salts were compared, the normal being too dark in colour.

Ferric salts taken as a whole yielded very remarkable results. Thus the sulphate forms only slightly coloured solutions, so they could not be compared. Ferric ammonium citrate proved to give exceedingly dark solutions, the colour of the decinormal compared with that of decinormal ferric chloride taken as 100 being 378.10, or nearly forty times as dark. All the values of the ferric salts are calculated for decinormal solutions, as in some cases the normal solutions were too dark to be compared. With ferric acetate and ferric ammonium citrate even the decinormal solutions were too dark for accurate comparison, so 100 litre solutions were made use of, and the values calculated from the results obtained with these. The acetate gave the next highest colour value, viz., 2147.0. The value is thus very much greater than even that found for copper acetate. The value for ferric citrate was found to be about 550, and for ferric tartrate about 350.

As will be shown later on, no proper colour comparison is possible between the solutions of these salts. Ferric oxalate and acid ferric citrate solutions could not be compared, as they are greenish yellow in colour. Thus all the organic ferric salt solutions it was possible to examine had values very much greater than that of ferric chloride. The reason of this is probably the same as that given to account for the large colour value of copper acetate solution.

On endeavouring to compare solutions of neutral ferric chloride with those of acid ferric chloride, ferric tartrate, and ferric citrate, very peculiar results were obtained. Thus it was found that the relation of the volumes of these liquids required to produce the same tint varied according to the thickness of the layer of ferric chloride solution they were compared with.

In the following table are given the colour effects of layers, 1 to 3 c.m. in thickness, of solutions of each salt compared with layers of equal thickness of acid ferric chloride solution taken as 100.

Thickness of layer of solution in c.m.	Colour effect of solution of—		
	Ferric chloride.	Ferric tartrate.	Ferric citrate.
1	39.0	154.7	255.0
1.5	49.6	185.3	285.1
2	58.8	213.0	312.0
2.5	67.5	227.5	339.1
3	72.4	230.6	349.7

As former experiments showed that the colour effect of acid ferric chloride solution increases proportionately to

the thickness of the layer of liquid viewed, it follows that the colour effects of the solutions of these three salts increase in a greater proportion than that of the thickness of the layers. Thus a layer of ferric chloride solution 3 c.m. in thickness has a colour effect nearly six times as great as a layer 1 c.m. in thickness, instead of only three times as great. These variations must be in some way due to the presence of free ferric oxide in the solutions.

The above results show that ferric tartrate and ferric citrate solutions also contain considerable quantities of ferric oxide, though not nearly so much as neutral ferric chloride solution. As on comparing together solutions of neutral ferric chloride, ferric ammonium citrate, and ferric acetate, no variations depending on the thickness of the layers of liquid examined were noticed, it follows that solutions of these two salts must contain as large quantities of ferric oxide in suspension as those of neutral ferric chloride. Now ferric ammonium citrate solution was found to afford scarcely any change at all in colour effect on dilution. There are probably, therefore, two opposite changes going on within it at the same time on dilution; one, a decomposition with formation of ferric oxide and an increase of colour effect; the other, a partial dissociation of the salt into ferric citrate and ammonium citrate, attended by a great decrease of colour effect.

Of the other salt solutions examined none could be compared together but those of potassium bichromate and chromium trioxide. If the colour effect of decinormal potassium bichromate solution be taken as 100, that of chromium trioxide is 23.2, or less than a fourth as great. Taken as a whole we see that the colour effects of organic salts are the greatest, those of chlorides next, then those of sulphates, and lastly those of nitrates. The colour effects of salts bear a considerable resemblance to the decrease of colour their solutions undergo on dilution. Thus those of organic salts show the greatest decrease on dilution, with the exception of uranyl acetate solution, which shows less decrease than any of the uranyl salts, and also less colour effect. Ferric citrate and tartrate solutions are also exceptions, but, as has been shown, their increase in colour on dilution is due to the formation of ferric oxide. Chlorides, with the exception of cupric chloride, show the next greatest colour decrease on dilution of their solutions. Cupric nitrate solution, which shows a greater colour decrease on dilution than solutions of either the chloride or the sulphate, also possesses a greater colour effect than these two solutions.

Nitrate solutions show a slightly greater decrease than sulphate solutions, although their colour effects are rather smaller. This is even the case with uranyl nitrate, although the colour effect of the sulphate is twice as large. This, in fact, forms the only marked exception to the otherwise general resemblance. The resemblance is manifestly much too great to be due to mere chance, and there is every reason to suppose it is due to the solutions with a greater colour effect containing the salts in a less dissociated state than those with a less colour effect, so that on dilution they decrease in colour effect or undergo dissociation to a greater degree.

The study of the colourimetric relations of solutions of salts at various dilutions and temperatures has thus been shown to give support to the electrolytic dissociation theory on the one hand, and to the hydrate theory on the other. Inasmuch as many and distinct proofs of the correctness of both these different theories on the nature of solution have been advanced, and as at first sight they appeared to be totally contrary to one another, the supporters of each theory tended rather to the opinion that the theory of the opposite party was quite incorrect. It is hoped that these experiments may be taken to indicate the possibility of both theories being correct. It would seem, therefore, that whilst salts in hot or very concentrated solutions exist in great part as anhydrous molecules, or as hydrates containing only small numbers of water molecules, they are also to a certain extent dissociated into their ions. In moderately dilute solutions

they are more dissociated, and at the same time the hydrates present contain more water molecules. In very dilute solutions the salts are totally dissociated into their ions, and no hydrates exist at all in solution. There is every probability that hydrates are completely decomposed at extremely dilute solutions, for it is evident that as a solution gets more and more dilute, and the hydrates in it contain more and more water molecules, the bonds which hold the salt molecule to the water molecules must become more and more feeble, till at last they dwindle down to nothing, and so the hydrates no longer have an existence.

Summary.

The chief conclusions arrived at in this paper are as follows:—

1. Almost all the solutions of the thirty-five coloured salts examined show considerable decrease in colour effect on dilution, due in all probability to dissociation taking place. The only exceptions are certain chromium derivatives, the colour of whose solutions, on gradual dilution, either remains constant or increases slightly. When their solutions are suddenly diluted, different colour values are obtained. Potassium permanganate solution only shows a very slight decrease in colour on dilution. Taken as a whole ferric salts show the greatest decrease in colour effect on dilution of their solutions, then cobalt salts, then uranium salts, and then nickel and cupric salts. Generally also organic salts show the most decrease of colour on dilution, chlorides less, nitrates still less, and sulphates the least.

2. All solutions of salts, with the exception of those of certain chromium derivatives, and perhaps of potassium permanganate, increase considerably in colour effect on being heated. The amount of colour increase depends on (1) the nature of the base of the salt, ferric salt solutions being most affected by temperature, then those of cobalt and uranium, and then those of copper and nickel; (2) on the nature of the acid radicle, chlorides being most affected, nitrates next, and sulphates least; (3) on the degree of dilution of the solution, sulphates being most affected in their decinormal solutions and least in their centinormal, whilst chlorides are most affected in their normal solutions and least in their centinormal. The results obtained for the effect of temperature on the colours of salt solutions are without exception in favour of the hydrate theory of the nature of solution.

3. On comparing solutions of different salts together as to colour effect, it is found that the values obtained bear considerable resemblance to the amounts of decrease of colour the solutions undergo on dilution, organic salts possessing the greatest colour effect, chlorides a lesser effect, sulphates and nitrates a still smaller colour effect. The results obtained as a whole indicate that dissociation takes place in solutions on the one hand, and hydrates are formed on the other, so it would seem that salts exist in solution in both these conditions at the same time.

ON AN APPARENT RELATION OF ELECTROMOTIVE FORCE TO GRAVITY.*

By Dr. G. GORE, F.R.S.

In a research on "A General Relation of Electromotive Force to Equivalent Volume and Molecular Velocity of Substances" (*Proc. Birm. Phil. Soc.*, 1892, vol. viii., pp. 63—138; *Electrical Review*, vol. xxx., pp. 693, 722, 755, 786), I have demonstrated, by means of a large number and variety of experimental measurements, that the dilution of the liquid of a voltaic cell by means of water or alcohol, the solution of either the positive metal or the

negative one by means of mercury, the dilution of either of these amalgams by means of mercury, or the dilution of one solid metal by means of another in an alloy, is universally attended by an increase of mean electromotive force of the diluted and diluting substances beyond the calculated amount, and therefore of the actual electromotive force of the diluted one (that of the diluent being very little affected), provided that no chemical union of the diluted and diluting substances occurs. If, however, chemical union does occur, this gain of electromotive force is diminished, or converted into a loss which is larger in proportion as the union is more intimate.

In these experiments, by the act of solution or dilution, the molecules of the active or diluted substance are separated farther apart by those of the neutral or diluting one, and acquire greater freedom of motion, whilst those of the diluent approach only slightly nearer together, and do not perceptibly affect the result.

It is generally admitted that the particles of all bodies are in an incessant state of motion, that this motion is the *vis viva* or energy contained in the substance, and that the laws of motion apply equally to the smallest as to the largest bodies. If now we regard each molecule of the active substance as vibrating like a pendulum, its movements must obey the law of falling bodies, and the larger the degree of freedom of motion the greater the arc of vibration, the larger the fall, and the greater the velocity of motion. And, as in the above mentioned experiments the volta electromotive force of substances generally has been proved to vary directly as the degree of molecular freedom, it must also, according to this view, be directly related to, and dependent upon, the velocity of molecular motion and the law of gravity in the above manner.

A METHOD FOR THE DETERMINATION OF BARIUM IN THE PRESENCE OF CALCIUM AND MAGNESIUM.*

By F. W. MAR.

THE recent investigation by Prof. R. Fresenius (*Zeit. f. Anal. Chem.*, xxx., 593) of the value of the various methods which have been proposed for the separation of barium and calcium, shows that but two of the methods tested by him are sufficiently accurate for good analytical work, and even with these it is necessary to make two treatments in order to obtain a complete separation. The method here described may therefore be of interest, and, by reason of its rapidity and accuracy, may prove valuable, although since the publication of the work of Fresenius another method (P. E. Browning, *Am. Jour. Sci.*, xliii., p. 314) has been published from this laboratory which, in point of accuracy, leaves little to be desired.

It has long been known that barium chloride is insoluble to a marked degree in concentrated hydrochloric acid, but the difficulty of filtering off the strong acid has in the past prevented the determination of the exact amount of this insolubility, and for the same reason the reaction has not been available for quantitative use. Since the invention of the Gooch crucible, however, the treatment of such strong acid filtrates has become a matter of the greatest ease, and it seemed worth while to investigate the limits of the insolubility of barium chloride in the strong acid and to ascertain whether the reaction might not be of use in the separation of barium from calcium and magnesium, the chlorides of which are soluble in the strong acid.

The barium chloride used in the following experiments was the pure crystallised chloride containing two molecules of water. The calcium salt was the pure fused chloride, and the magnesium salt was the pure crystal-

* From the *Philosophical Magazine* for September, 1892.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xliii., June, 1892.

lised magnesium chloride dried at 50° C. As the two latter were not determined in the experiments it was not necessary to know the composition of the salts used as regards hygroscopic moisture. Attention was first given to determining the solubility of barium chloride in hydrochloric acid.

Series A.

Exp.	BaCl ₂ .2H ₂ O. Grm.	Water. C.m. ³	HCl. C.m. ³	Total filtrate. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
1.	0.5024	5	20	—	0.4241	0.0041
2.	0.5084	5	20	—	0.4304	0.0030
3.	0.5099	2	25	—	0.4320	0.0027
4.	0.5033	2	25	90	0.4251	0.0039
5.	0.5047	2	25	52	0.4247	0.0055
6.	0.5065	2	50	115	0.4257	0.0060
7.	0.5008	2	50	75	0.4218	0.0051
8.	0.5011	2	50	93	0.4220	0.0051
9.	0.5024	2	75	123	0.4246	0.0037

The experiments in Series A were made as follows:—The barium salt was weighed out, placed in a small beaker, and dissolved in the amount of water indicated. The barium was then precipitated as the anhydrous chloride by adding, gradually at first, the amount of hydrochloric acid shown. After standing for five or ten minutes the precipitates were filtered off upon asbestos in Gooch crucibles, washed with concentrated hydrochloric acid, dried sometimes over a low flame (at about 150°—200° C.) and sometimes in an air bath heated to 165° C., and weighed. In several cases the total filtrate was measured and the volume is given in the tabular statement. The results show a considerable solubility amounting to about 1 part in 8000 under the conditions given.

Series B.

Exp.	BaCl ₂ .2H ₂ O. Grm.	Water. C.m. ³	HCl. C.m. ³	Total filtrate. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
10.	0.5057	2	25	75	0.4268	0.0042
11.	0.5017	5	50	90	0.4198	0.0078
12.	0.5068	3	50	100	0.4235	0.0085
13.	0.5019	2	100	144	0.4186	0.0082

The experiments in Series B were conducted similarly to those of Series A, except that the precipitates were allowed to stand twenty-four hours before filtration. The loss due to solubility was, as is shown by the table, greater than before, due doubtless to the escape of hydrochloric acid gas from the solution.

Series C.

Exp.	BaCl ₂ .2H ₂ O. Grm.	Water. C.m. ³	HCl. C.m. ³	Alcohol. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
14.	0.5011	3	25	15	0.4228	0.0043
15.	0.5096	2	25	10	0.4278	0.0066

The experiments of Series C were conducted in the same manner as those of Series A, except that the amount of absolute alcohol indicated was added after the precipitation by hydrochloric acid. The results show that the alcohol neither decreased nor increased the amount of the solubility of the chloride.

Series D.

Exp.	BaCl ₂ .2H ₂ O. Grm.	HCl. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
16.	0.5019	50	0.4249	0.0029
17.	0.5020	50	0.4257	0.0022
18.	0.5020	50	0.4255	0.0024
19.	0.5016	50	0.4259	0.0017
20.	0.5022	50	0.4267	0.0014

In the experiments of Series D the weighed barium chloride was placed in an Erlenmeyer beaker and dissolved in 4 or 5 c.c. of water. The indicated amount of acid was then added, and a stream of hydrochloric acid gas was passed for two hours into the cooled mixture. The precipitates were then treated as in the former experi-

ments. The results show that even in the strongest possible solution, at the ordinary temperature, of hydrochloric acid barium chloride is soluble to a considerable degree, this solubility amounting according to the first three experiments of the series to about one part in 20,000. In Experiments 18 and 19 ten c.c. of absolute ether were added to the solution before passing in the hydrochloric acid gas. The results showed that the ether seemed to decrease the solubility of the barium salt, and therefore the experiments of the following series were undertaken.

Series E.

Exp.	BaCl ₂ .2H ₂ O. Grm.	HCl. C.m. ³	Ether. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
21.	0.5008	50	10	0.4267	0.0002
22.	0.5002	50	10	0.4257	0.0007
23.	0.4999	50	10	0.4252	0.0009
24.	0.4999	50	10	0.4258	0.0003
25.	0.5003	25	25	0.4259	0.0005
26.	0.5002	25	5	0.4262	0.0002
27.	0.5099	25	5	0.4344	0.0003
28.	0.5003	25	5	0.4261	0.0003

The experiments of Series E were conducted as follows. The amount of barium salt specified was dissolved in the least convenient amount of hot water (about 2 c.m.³) and precipitation was brought about by adding the indicated amount of concentrated hydrochloric acid. The beaker containing the precipitate was then placed in cold water and the amount of ether shown in the tables was added and mixed with the solution by thorough stirring. After standing for five or ten minutes the precipitate was filtered off and washed with concentrated hydrochloric acid containing about ten percentum by volume of absolute ether and dried, sometimes in an air-bath at 165°—170° C. and at others over a radiator giving a temperature of 175°—200° C. A constant weight was more quickly obtained by the latter method, and it was used exclusively in the experiments of the subsequent series. In using it a low heat was used at first and the temperature was not increased until the precipitate was moderately dry. The results show that barium chloride is practically insoluble in a mixture of hydrochloric acid and ether containing about one-sixth by volume of the latter. The average solubility calculated from the experiments given is one part in 122,000. The actual solubility is less than this, since no account was taken of the volume of the washings, which were at least equal to the original filtrates.

Series F.

Exp.	BaCl ₂ .2H ₂ O. Grm.	CaCl ₂ . Grm.	HCl. C.m. ³	Ether. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
29.	0.5001	0.5	50	10	0.4250	0.0013
30.	0.4999	0.5	50	10	0.4250	0.0011
31.	0.5005	0.5	25	25	0.4260	0.0006
32.	0.5002	0.42	25	5	0.4258	0.0004
33.	0.5001	0.5	25	5	0.4255	0.0008
34.	0.5005	0.5	25	5	0.4251	0.0015
35.	0.5001	0.5	25	5	0.4254	0.0009
36.	0.5001	0.5	25	5	0.4258	0.0005
37.	0.5003	0.5	25	5	0.4261	0.0004
38.	0.1002	3.0	25	5	0.0842	0.0010
39.	0.0107	3.0	25	5	0.0080	0.0005
40.	0.5100	0.5	25	5	0.4328	0.0020

Series F was undertaken to test whether the mode of precipitating barium used in the preceding series would be of use in the separation of the barium from calcium. The experiments were conducted as in Series E, except that the calcium salt was dissolved with the barium chloride. It was necessary to use more water than in Series E to effect solution, but as the barium salt was uniformly the last to dissolve, the effect was practically the same as before. The results show that mixtures of barium and calcium in all proportions are perfectly sepa-

rated by this method, 0.020 grm. of barium chloride being separated with accuracy from 3 grms. of calcium chloride. The calcium does not show the slightest tendency to come down with the barium, and those experiments in which separation was effected by the use of 25 c.m.³ of hydrochloric acid and 5 c.m.³ of ether gave rather better results than those in which double this volume was employed. It is better not to let the precipitations stand too long before filtration, even if kept cold, as the hydrochloric acid evaporates from the solution, and experiments in which filtration was delayed for about two hours (e.g., Experiments 33, 34, 35) show a rather larger loss than the average. That there is no advantage in increasing the amount of ether over the proportions used above is shown by Experiment 31, which is comparable with Experiment 25. In the case of Experiment 40, in which no ether was used, the result is comparable with the experiments of Series A. The precipitate was washed, however, with the mixture of hydrochloric acid and ether.

Series G.

Exp.	BaCl ₂ ·2H ₂ O. Grm.	MgCl ₂ ·6H ₂ O. Grm.	HCl. C.m. ³	Ether. C.m. ³	BaCl ₂ . Grm.	Loss. Grm.
41.	0.4999	0.5	25	5	0.4233	0.0007
42.	0.5000	0.5	25	5	0.4257	0.0005
43.	0.1002	3.0	25	5	0.0844	0.0008
45.	0.0100	3.0	25	5	0.0077	0.0008

The experiments of Series G were made in exactly the same manner as those of Series F, except that varying amounts of magnesium chloride were present instead of the calcium salt. The results are uniform and exact, and indicate that barium may be separated from magnesium when the two are present in any proportion. It is probable that if magnesium chloride were present in an amount larger than 3 grms. in 30 c.m.³, it would be necessary to make two treatments, as under those circumstances it shows a slight tendency to precipitate. The amount of mixed salts present should always, therefore, be kept below this limit.

Recapitulation.—Barium chloride is soluble to an extent not exceeding one part in 20,000 in pure concentrated hydrochloric acid, but the solubility increases very rapidly with the diminution in the strength of the acid. In concentrated hydrochloric acid containing ether it is soluble to an amount not exceeding one part in about 120,000. To utilise this fact for the separation of barium from calcium and magnesium, the chlorides of the earths are dissolved in the least possible amount of boiling water, and precipitated by 25 c.m.³ of concentrated hydrochloric acid, with the addition of 5 c.m.³ of absolute ether after cooling. The acid should be added drop by drop, at first allowing the precipitate formed to re-dissolve as long as possible, as the precipitate is thus obtained in a coarse crystalline condition and filters very quickly, and is less liable to include foreign matter. After standing a few minutes the precipitate is to be filtered in a Gooch crucible, washed with hydrochloric acid containing about 10 per cent of ether, and dried at 150°–200° C. The method is accurate and rapid, and possesses the further advantage when a number of determinations are to be made that the precipitate may be dissolved off the felt by a little water, and, after ignition, the crucible and felt may be used again without re-weighing. A felt upon which half a dozen precipitates were weighed did not change its weight to the extent of one-tenth of a mgrm. The fumes of the strong acid cause no inconvenience if the filtration is performed in front of a good flue. A gas flame may be used in the flue without danger from the ether, which seems to be firmly held by the hydrochloric acid. A flame was used to increase the draught in all of the experiments given, and with entire safety, even when the filtrate contained 50 per cent by volume of ether.

The author wishes in concluding to acknowledge his indebtedness to Prof. Gooch for many helpful suggestions freely given in the course of the investigation.

NOTES ON THE ANALYSIS OF THE NITRO-EXPLOSIVES.*

By P. GERALD SANFORD, F.I.C.. F.C.S.

Now that the various forms of nitro compounds are gradually replacing the older forms of explosive agents, both for blasting purposes and also as a propulsive agent, perhaps some notes upon the methods for their analysis and examination, that I have used and found to work satisfactorily, may be of service to other chemists who may be engaged upon similar work. The class of compounds that have come into the most extended use for the purposes of mining, blasting, &c., are the nitro-glycerin compounds, more especially the gelatin compounds, composed of nitro-cellulose and nitro-glycerin, and generally containing some admixture of nitrates and wood pulp, or similar materials.

Kieselguhr Dynamite.

This material generally consists of 75 per cent nitro-glycerin and 25 per cent of the infusorial earth Kieselguhr. The analysis is very simple, and may be conducted as follows:—Weigh out about 10 grms. of the substance, and place over calcium chloride, in a desiccator, for some six to eight days, and then re-weigh; the loss in weight gives the moisture; this will generally be very small, probably never more than 1 per cent. The dry substance may now be wrapped in filter-paper, the whole weighed, and the nitro-glycerin extracted in the Soxhlet apparatus with ether. The ether should be distilled over at least twenty-four times. I have found, however, that results may be obtained much quicker, and quite as accurate, by leaving the dynamite in contact with ether in a small Erlenmeyer flask for some hours,—leaving it over night is better,—and then decanting, and again allowing the substance to remain in contact with the ether for a few hours, and finally filtering through a weighed filter, drying at 100° C., and weighing. This gives the weight of Kieselguhr. The nitro-glycerin must be obtained by difference, as it is quite useless to evaporate down the ethereal solution to obtain it, as it is itself volatile to a very considerable extent at the temperature of evaporation of the ether, and the result, therefore, will always be much too low. An actual analysis of Kieselguhr dynamite gave:—Moisture, 0.92 per cent; Kieselguhr, 26.15 per cent; and nitro glycerin, 72.93 per cent, this last being obtained by difference.

Gelatin Compounds.

The simplest of these compounds is, of course, blasting gelatin, as it consists of nothing but nitro-cotton and nitro-glycerin, the cotton being dissolved in the glycerin to form a clear jelly, the usual proportions being about 92 per cent of nitro glycerin to 8 per cent of nitro-cotton, but the cotton is found as high as 10 per cent in some gelatins. Gelatin dynamite and gelignite are blasting gelatins with varying proportions of wood pulp and saltpetre (KNO₃), mixed with a thin blasting gelatin. The method of analysis is as follows:—Weigh out about 10 grms. of the substance, previously cut up in small pieces, and place over calcium chloride in a desiccator for some days. Re-weigh; the loss equals moisture. This is generally very small. The dried sample is then transferred to a small thistle-headed funnel which has been cut off from its stem, and the opening plugged with a little glass wool, and round the top rim of which a piece of fine platinum wire has been fastened, in order that it may afterwards be easily removed from the Soxhlet tube. The weight of this funnel and the glass wool must be accurately known. It is then transferred to the Soxhlet tube and exhausted with ether, which dissolves out the nitro-glycerin. The weighed residue must afterwards be

* *Journal of Analytical and Applied Chemistry*, vol. vi., No. 6, June, 1892.

treated with ether-alcohol to dissolve out the nitro-cotton.

But the more expeditious method is, perhaps, to transfer the dried gelatin to a conical Erlenmeyer flask of about 500 c.c. capacity, and add 250 c.c. of a mixture of ether-alcohol (2 ether to 1 alcohol), and allow to stand over night. (Sometimes a further addition of ether-alcohol is necessary, but not often). The undissolved portion, which consists of the wood pulp, and potassium nitrate, and other salts, is then filtered off, dried, and weighed.

Solution.—The ether-alcohol solution contains the nitro-cotton and the nitro-glycerin in solution. To this solution add excess of chloroform, when the nitro-cellulose will be precipitated in a gelatinous form. This should be filtered off through a linen filter, and allowed to drain. It is useless to attempt to use a filter pump, as it generally causes it to set solid. The precipitated cotton should then be re-dissolved in ether-alcohol, and again precipitated with excess of chloroform. This precaution is absolutely necessary, as otherwise the results will be much too high, owing to the gelatinous precipitate retaining very considerable quantities of nitro-glycerin. The precipitate is then allowed to drain as completely as possible, and finally dried in the air-bath at 40° C. until it is easily detached from the linen filter by the aid of a spatula, and then transferred to a weighed watch-glass, replaced in the oven, and dried at 40° until constant in weight. The weight found, calculated upon the 10 grms. taken, gives the percentage of nitro cellulose.

The residue left after treating the gelatin with ether-alcohol is, in the case of blasting gelatin, very small, and will probably consist of carbonate of soda. It should be dried at 40° C., and weighed, but in the case of either gelignite or gelatin dynamite this residue should be transferred to a beaker and boiled with distilled water, and the water decanted three or four times, and the residue finally transferred to a tared filter and washed for some time with hot water. The residue left upon the filter is wood pulp. This is carefully dried at 40° C., until constant, and weighed. The solution and washings from the wood are evaporated down in a platinum dish and dried at 100° C. in the oven, and weighed. It will consist of the potassium nitrate, and any other mineral salts, such as carbonate of soda, which should always be tested for by adding a few drops of nitric acid and a little water to the residue, and again evaporating to dryness and re-weighing. From the difference in weight the soda can be calculated, sodium nitrate having been formed.

The nitro-glycerin is best found by difference, but, if desired, the solutions from the precipitation of the nitro-cellulose may be evaporated down upon the water-bath at 30° to 40° C., and finally dried over CaCl_2 until no smell of ether can be detected, and the nitro-glycerin weighed. It will, however, always be much too low. An actual analysis of a sample of gelatin dynamite gave the following result:—

Nitro-cellulose	3.819 per cent.
Nitro-glycerin	66.691 "
Wood pulp	16.260 "
KNO_3	12.890 "
Water	0.340 "
100.000	

This sample was probably intended to contain 30 per cent of absorbing material to 70 per cent of explosive substances.

Gun-Cotton.—Collodion cotton, and other forms of nitro-cellulose, i.e., the hexa-nitro-cellulose and lower nitro bodies. The first thing upon opening a case of wet gun-cotton, or in receiving a sample from "the poacher," that requires to be determined, is the percentage of water that it contains; it is best done by weighing out about 1000 grms. upon a paper tray, which has been previously dried in the oven at 100° C. for some time and become

constant in weight. The tray full of cotton is then placed in a water oven, kept at 100° C., and dried as long as it loses water. The loss gives the percentage of water. It varies from 20 to 30 per cent, as a rule, in what is known as wet cotton.

The Solubility Test.—The object of this test is to ascertain, in the case of gun-cotton, the percentage of soluble (penta and lower nitrates) cotton that it contains, or, in the case of soluble cotton, the quantity of gun-cotton. The method of procedure is as follows:—Five grms. of the sample, which has been previously dried at 100° C. and afterwards exposed to the air for two hours, is transferred to a conical flask, and 250 c.c. of ether-alcohol added. The flask is then corked and allowed to digest, with repeated shaking, for two or three hours. The whole is then transferred to a linen filter, and, when the solution has passed through, the filter is washed with a little ether and pressed in a screw-press between folds of filter-paper. The sample is then returned to the flask, and the previous treatment repeated, but it will be sufficient for it to digest one hour the second time. The filter is then opened up, and the ether allowed to evaporate. The gun-cotton is then removed from the filter and transferred to a watch-glass, and dried in the water oven at 100° C. When it is dry it is exposed to the air for two hours and weighed. It equals the amount of gun-cotton and unconverted cotton. In the 5 grms. the non-nitrated cellulose must be determined in a separate 5 grms. and deducted.

Estimation of the Non-nitrated Cotton.

However well the cotton has been nitrated, it is almost certain to contain a small quantity of non-nitrated or unconverted cotton. This can be determined thus:—Five grms. of the sample are boiled with a saturated solution of sodium sulphide, and then allowed to stand for forty-eight hours, and afterwards filtered or decanted, and again boiled with fresh solution of sulphide, and again filtered, dried, and weighed. The residue is the cellulose that was not nitrated. It should be ignited, and the weight of the ash deduced from the previous weight.

Alkalinity.

Five grms. of the air-dried and very finely divided sample are taken from the centre of the slabs or discs, and digested with about 20 c.c. of $\frac{1}{4}$ hydrochloric acid, and diluted with water to about 250 c.c., and shaken for about fifteen minutes. The liquid is then decanted and washed with water until the washings no longer give an acid reaction. The solution, together with the washings, are then titrated with $\frac{1}{4}$ sodium carbonate, using litmus as indicator.

Nitrogen.

The estimation of the percentage of nitrogen in a sample of gun-cotton or collodion cotton is perhaps of more value, and affords a better idea of its purity and composition than any of the foregoing methods of examination, and, taken in conjunction with the solubility test, it will generally give the analyst a very fair idea of the composition of his sample. If we regard gun-cotton as the hexa-nitro-cellulose $\text{C}_{12}\text{H}_{14}\text{O}_4(\text{ONO}_2)_6$, the theoretical amount of nitrogen required for the formula is 14.14 per cent; and in the same way for collodion cotton, which consists of the lower nitrates, that is the penta and tetra-nitro bodies, the theoretical nitrogen is 11.11 per cent and 6.76 per cent respectively; so that, if in a sample of gun-cotton the nitrogen falls much lower than 14 per cent, it probably contains considerable quantities of the lower nitrates, and perhaps some non-nitrated cellulose as well ($\text{C}_6\text{H}_{10}\text{O}_5$), which, of course, would also lower the percentage of nitrogen. The most expeditious method of determining the nitrogen in these nitro-bodies is by the use of Lunge's nitrometer, and the best way of working the process is as follows:—Weigh out with the greatest care 0.6 gm. of the previously dried cotton in a

small weighing bottle of about 15 c.c. capacity, and carefully add 10 c.c. of concentrated sulphuric acid from a pipette. Allow to stand until all the cotton is dissolved. The nitrometer should be of a capacity of 150 to 200 c.c., and should contain a bulb of 100 c.c. capacity at the top, and should be fitted with a Greiner and Friederich's three-way tap. When the nitro-cotton has entirely dissolved to a clear solution, raise the pressure of the nitrometer, so as to bring the mercury in the measuring tube close up to the tap. Open the tap, in order to allow of the escape of any air-bubbles, and clean the surface of the mercury and the inside of the cup with a small piece of filter-paper. Now close the tap, and pour the solution of the nitro-cotton into the cup. Rinse out the bottle with 15 c.c. of concentrated sulphuric acid, contained in a pipette, pouring a little of the acid over the stopper of the weighing bottle, in case some of the solution may be on it. Now lower the pressure tube a little, just enough to cause the solution to flow into the bulb of the measuring tube when the tap is slightly opened. When the solution has run in almost to the end, turn off the tap, wash down the sides of the bottle, and add to the cup of the nitrometer; allow it to flow in as before, and then wash down the sides of the cup with 10 c.c. of sulphuric acid, adding little by little, and allowing each portion added to flow into the bulb of the nitrometer before adding the next portion. Great care is necessary to prevent air-bubbles obtaining admission, and if the pressure tube is lowered too far the acid will run in with a rush and carry air along with it. The solution being all in the measuring tube, the pressure tube is again slightly raised, and the tube containing the nitro-cotton solution shaken for ten minutes with considerable violence. It is then replaced in the clamp, and the pressure relieved by lowering the pressure tube, and the whole apparatus allowed to stand for twenty minutes, in order to allow the gas evolved to assume the temperature of the room. A thermometer should be hung up close to the bulb of the measuring tube. At the end of the twenty minutes the levels of the mercury in the pressure and measuring tubes are equalised, allowing about three inches of the sulphuric acid to one inch of mercury, and the final adjustment obtained by slightly opening the tap on the measuring tube (very slightly), after first adding a little sulphuric acid to the cup, and observing whether the acid runs in or moves up. This must be done with very great care. When accurately adjusted it should move neither way. Now read off the volume of the NO gas in c.c. from the measuring tube. Read also the thermometer suspended near the bulb, and take the height of the barometer in millimetres. The calculation is very simple.

Example Collodion Cotton.

0.6 grm. taken. Reading on measuring tube = 114.6 c.c. NO. Barometer, 750 m.m. Temperature, 15° C.

Since 1 c.c. NO = 0.6272 grm. N., and correcting for temperature and pressure by the formula $760 \times (1 + d^2)$ ($d = 0.003665$) for temperature of 15° = 801.78; then—

$$\frac{114.6 \times 100 \times 750 \times 0.6272}{801.78 \times 0.6} = 11.22 \text{ per cent N.}$$

Theory = 11.11 per cent for $C_6H_8(NO_2)_2O_5$.

The following is the analysis of a good sample of collodion cotton suitable for the manufacture of blasting gelatin, &c.

Soluble cotton	= 99.118 p.c.	} = Nitrogen = 11.67 p.c.
Gun cotton	= 0.642 "	
Non nitrated cotton	= 0.240 "	

Total ash = 0.25 "

The nitrogen in nitro-glycerin may, of course, be determined by the nitrometer, but in this case it is better to take a much smaller quantity of the substance,—from 0.1 to 0.2 grm. is quite sufficient. This will give from 30 to 60 c.c. of gas, and therefore a measuring tube without a 100 c.c. bulb must be used.

Example.

0.1048 grm. nitro-glycerin taken; Barometer, 761 m.m.; Temperature, 15° C.; gave 32.5 c.c. NO.

$$\frac{32.5 \times 100 \times 761 \times 0.6272}{801.78 \times 0.1048} = 18.46 \text{ per cent N.}$$

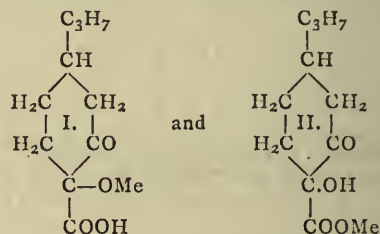
Theory for $C_{13}H_{14}O_4(ONO_2)_6 = 18.50$ per cent.

METHYL SALTS OF CAMPHORIC ACID.*

By JAMES WALKER, Ph.D., D.Sc.

THE author prepared the two isomeric hydrogen methyl camphorates, and investigated their electrolytic conductivity with a view to testing the validity of Friedel's formula for camphoric acid. The substances he obtained are identical with those prepared by Brühl.

According to Friedel, camphoric acid forms two hydrogen methyl salts having the formulæ—



Now these substances ought to be widely different in their strength as acids, and consequently in their dissociation constants as determined from the electrolytic conductivity of their solutions. I. should have a constant greater than that of camphoric acid itself, while II. should have a constant ten times less at least than that of camphoric acid. As a matter of fact, the constants of the two isomeric substances are very nearly the same, and equal to about half the constant of camphoric acid, which is precisely what should be expected if camphoric acid were a dicarboxyl acid (compare Walker, *Journ. Chem. Soc.*, 1892, p. 715).

THE RED CHALKS OF ENGLAND.

By WILLIAM JOHNSTONE,
Emeritus Fellow of the Institute of Chemistry.

HAVING had occasion some time ago to make a number of analysis of the English chalks, both white and red, and as I know they will be of interest to several of your readers, I append the results obtained from the red chalks of Yorkshire, reserving for a future communication those of Norfolk.

No. 1.—From Speeton Gap. From top red bed, 3 ins. to 2 ft. 8 ins. thick.

No. 4.—From Speeton Gap. From upper of lower red beds.

No. 5.—From Speeton Gap. From lower of lower red beds.

No. 8.—From Warter. From Gravel Pit.

No. 10.—From Millington. From Millington Wolds.

No. 13.—From Speeton Cliff. From Red Marl Bed.

No. 15.—From Speeton Cliff. From upper of lower red beds.

I have to thank my assistants, Messrs. H. E. Lindley, E. J. Philbrick, J. J. Hogg, and C. R. Lidgy, for assistance in the work.

* Read before the British Association, Edinburgh Meeting, 1892, Section B.

	No. 1.	No. 4.	No. 5.	No. 8.	No. 10.	No. 13.	No. 15.
SiO ₂	10'01	12'42	30'00	6'08	7'27	39'94	5'48
Fe ₂ O ₃	2'35	3'95	6'50	3'50	4'10	3'75	0'95
Al ₂ O ₃	1'60	2'07	2'35	1'25	2'50	2'67	0'65
MnO	trace	trace	trace	trace	0'62	1'20	trace
CaCO ₃	80'59	79'87	60'21	86'37	80'89	48'31	88'78
CaSO ₄	3'78	0'84	0'24	0'76	2'64	1'40	3'14
MgCO ₃	1'63	0'75	0'43	1'06	1'44	1'53	trace
	99'96	99'90	99'74	99'02	99'46	98'80	99'00

NOTICES OF BOOKS.

On the Organisation of Science; being an Essay towards Systematisation. By "A FREE LANCE." "Divide et Impera." London: Williams and Norgate.

WE have here a pithy and timely pamphlet. The "Free Lance" touches with the point of his weapon certain flaws in our present system—or, as he happily calls it, *unsystem*—of the cultivation of science, and gives suggestions for their removal. To give no scope for misunderstanding, we must premise that our author is not dealing with *education*. He is scrutinising our facilities for the further cultivation of science by those who are no longer pupils in the ordinary sense of the term, but have entered upon a career of research. He points out that they find in their way a number of difficulties which are capable of removal, but which in the meantime waste the opportunities and the resources of the aspirant.

These difficulties, which are donkeys, if not lions, in the way, are to be found in our scientific societies and our scientific journals. Instead of having "a place for everything, and everything in its place," we have for many a thing, if not for everything, several places.

Now, let us suppose a young *savant* desirous of taking up some particular subject. His first and most obvious task is to ascertain what, if anything, has been previously done in this direction. If he neglect this tedious duty he may simply be wasting his time and inditing an *Iliad post Homerum*; or he may fall into unintentional plagiarism, and may involve his colleagues in an "unerquicklich"—as the Germans call it—controversy on priority. Now to ascertain what has been already published—say, on a chemical subject—in England alone he will have to wade through the journals of the Chemical Society, possibly the *Philosophical Transactions*, as well as the *CHEMICAL NEWS*, the *Analyst*, the publications of the Society of Chemical Industry, the *Chemical Trades' Journal*, the *Pharmaceutical Journal*, the *Chemist and Druggist*, &c. All this means both time and money—requisites with which the inquirer is not always over-burdened.

As regards biology, the case is still worse, as we have not here space to show. "A Free Lance" therefore proposes—if we understand him aright—a decrease in the number of societies, and a restriction on the class of subjects admitted by each. He takes up his parable against the Zoological and the Entomological Societies as "robbing" the Linnean. Possibly our author knows the circumstances which led to the formation of the Entomological Society. It was felt as a grievance that the Linnean Society was too exclusively botanical, and the Zoological Society too vertebrate, and as the Articulata form, in number of species, the vast majority of the animal kingdom, if not of the entire organic world, and as they are more powerful for good and evil than the other zoological divisions, it was felt that entomology was fully entitled to an organisation of its own. The author's remarks on the "collectors"—especially of so-called "British"—are fully justified.

Upon the conduct of the Microscopical Society, "A Free Lance" might, without injustice, have spoken more emphatically. It is a case of "cross divisions." We have no right to classify Nature according to the instruments which we use in the study of her different departments.

Would it be wise to institute a Spectroscopical Society, or a Blowpipe Society?

Some of the author's strictures must at once be accepted as too well founded. Our recognised scientific societies would doubtless become more energetic if country members were allowed to take part in the election of council and officers by sending in their ballot-papers by post. Another point which he notices with disapproval is the very perfunctory character of the discussion. He suggests as a remedy that papers should be printed and distributed among the Fellows before being read. This, we must add, is done very successfully by the Victoria Institute.

On one important point the author does not touch. Not the least important step required towards the organisation of science is the dissociation of the so-called "Literary and Philosophical" societies of our large provincial cities. Here science is to a great extent crowded out by a medley of matter which is included under the name of literature, and which appropriates so large a share of time at the society's meetings, and of the space in its "Proceedings," that it would be to the advantage of science to dissolve partnership.

How sound are the views of "A Free Lance" will be seen from the following passage:—"I am concerned here with the intellectual feeding—or starving—of not the professional scientists only, but of that whole body of educated—really educated—outsiders that we may anticipate will presently exist when our 'educational' establishments shall have left off teaching Latin verse and Greek myths and instituted a scientific culture."

Space does not permit us to discuss all the many utterances in this pamphlet which merit careful consideration, but we trust it will be widely and thoughtfully read.

A Handy Book for Brewers; being a Practical Guide to the Art of Brewing and Malting, embracing the Conclusions of Modern Research which bear upon the Practice of Brewing. By HERBERT EDWARDS WRIGHT, M.A., author of "The Handbook for Young Brewers." London: Crosby Lockwood and Son, 1892.

To brewers of the olden time this book would seem an unintelligible curiosity. They were accustomed to obtain their results—intermingled, doubtless, with disastrous failures—by "rule of thumb." The experience of the observant brewer, backed by the traditions of the trade, was often a very safe guide to success, so long—but only so long—as all working conditions remained absolutely unaltered. But here was the difficulty. The quality of the water might change; the hops, even if always selected of one growth, might vary from season to season. But probably of all the materials used in industry yeast is the most mutable. It is only quite of late, as the result of a long and difficult course of microscopical research and biological experiment, that it has been found possible to obtain a pure and constant yeast.

By degrees, brewing has risen from a mere routine art to the rank of an important branch of technical chemistry. Our author places himself at the point of view indicated by Pasteur and Hansen and others. Here it must not be forgotten there is still abundant scope left for the ingenuity of the brewer.

The qualities of water and the determination of its

possible impurities are considered elaborately and fairly. The ammonia process, the permanganate method, and the tests of Heisch and Hansen are all described and criticised. The theory of previous sewage contamination is not accepted. The presence of sulphates in water is pronounced beneficial to the brewer. This view is quite in accordance with English practice, although in many Continental districts soft waters are preferred. Organic matter is, of course, pronounced as objectionable.

A very judicious caution is given in the chapter on planning a brewery. Says the author:—"Haylofts and oat-stores should on no account be anywhere near the fermenting-room, and it would be better if the prevalent winds did not blow from them towards the brewery. Hay teems with the spores of bacilli, and the light dust from corn is hardly less fertile, so that, if stores for them adjoin the fermenting-room, pure yeast is not to be expected."

Drains within the premises are also condemned. It is recommended that all waste waters and all matter capable of putrefaction should be carried out by means of deep wooden shoots.

This book will be found very useful, not merely to persons engaged in the fermentation trades, but to chemists who wish to place themselves in the brewer's point of view.

Treatise relative to the Testing of Water-wheels and Machinery; also of Inventions, Studies, and Experiments. With Suggestions from a Life's Experience. By JAMES EMERSON. Fourth Edition, 1892. Willimonssett: The Author.

THIS is one of the most singular books with which it has been our fate to come in contact. There are notices of improvements in the construction of turbines and other machinery. There are controversial passages anent rival inventors; there are denunciations of law and lawyers; of medicine and doctors; of colleges and their graduates; of over-education and its results; reports of trials or parts of trials in which the author shows an honest contempt for the system of examination and cross-examination; notes on marriage, divorce, and nudity, &c. There is literary criticism; the author stating that he would rather be the author of Pope's "Essay on Man" than of any other other English work! There are contemptuous notices of Shakspeare and of Darwin. There are comments on Christianity and on the clergy of all denominations, which in former days would have been considered to verge unpleasantly close upon blasphemy.

Of course, any criticism of such a work in the CHEMICAL NEWS is out of the question.

CORRESPONDENCE.

THE LUMINOSITY OF FLAME.

To the Editor of the Chemical News.

SIR,—In your report of Professor Smithell's very interesting paper on "Experiments on Flame" and the discussion which followed, Sir George Stokes is said to have stated that "he understood from Professor E. Frankland that the latter had abandoned the view that luminosity was due to dense hydrocarbon vapours." In this, Sir George has misinterpreted my views on the subject.

In a lecture on coal-gas delivered at the Royal Institution in 1867, and published in the *Journal of Gas Lighting*, I said "I do not mean to assert that the decomposition of the hydrocarbons is never complete in the gas flame, and that under no circumstances does a single particle of elementary carbon ever separate in such a flame; but I do maintain that the luminosity in a gas flame is almost entirely due, not to this source, but to the ignition of the very dense vapours which are produced at the expense of

the gaseous hydrocarbons contained in the coal-gas." To this statement I still substantially adhere.

Although the classical researches of Heumann leave no doubt that solid or liquid particles do exist in gas and candle flames, my own subsequent experiments, a description of which I hope shortly to publish, go to show that such particles do not constitute the chief, or even an important, source of luminosity in these flames.—I am, &c.,

E. FRANKLAND.

The Yews, Reigate,
Sept. 17, 1892.

DISINTEGRATING ALLOY OF IRON, ALUMINIUM, AND MANGANESE.

To the Editor of the Chemical News.

SIR,—In Mr. T. W. Hogg's interesting "Note on some Alloys of Iron, Aluminium, and Manganese" (CHEMICAL NEWS, vol. lxxvi., p. 140), his analysis of the disintegrating alloy accounts for only 94.29 per cent. "The deficiency," he says, "is no doubt due to oxygen, slight oxidation having taken place owing to the finely divided condition of the alloy." He evidently assumes oxidation to have been a consequence of disintegration, and not the cause thereof, as I imagine is the more likely. Were the disintegration due to some molecular change, then the fittest time for its accomplishment was when the alloy was at a red heat and its cohesive powers weakened. Whereas the twelve months required for its complete disintegration is more like the effect of slow atmospheric oxidation, hydration, or carbonation.

I have examined a few disintegrating compounds, and when air, moisture, and carbonic acid were excluded, these were quite permanent. Limey slag from manufacture of hematite iron often disintegrates or "falls," due to the hydration of CaO and oxidation of CaS contained in these slags. Firebricks that have been heated in contact with alkaline substance, and become saturated therewith, disintegrate into fine powder when exposed to the atmosphere.

Another instance I may cite is that of alkaline cokes perfectly stable at a red heat or when preserved dry, but crumbling slowly on exposure to weather.

In these cases I think it may be safely assumed that the substance acted upon by the atmosphere forms a minute network throughout the mass, and that the expansion of this on hydration, &c., is the cause of disintegration. In the alloy under consideration I can easily imagine an analogous action taking place, and the aluminium (although, it may be, forming some weak compound when molten) being thrown out when the mass cools, much in the same way as carbon is thrown out and forms a continuous network in ordinary pig-iron. However, it is to be hoped that Mr. Hogg will resume the investigation from this point of view, and publish his results in some future number, as it is rather a curious and interesting phenomenon.—I am, &c.,

GEORGE CRAIG.

Lugar Iron Works,
Cumnock, N.B.

Mining and Science Schools, Penzance.—Mr. H. Cavendish has been appointed Principal of the Penzance Mining and Science Schools in the place of Mr. H. Bailey. Mr. Cavendish is an Associate of the Royal School of Mines, where for three years he held a National Scholarship, and he also holds the honours certificates of the Science and Art Department in assaying, metallurgy, chemistry, principles of agriculture, &c. Mr. Cavendish has held the positions of Instructor of Assaying and Metallurgy at Onslow College, Chelsea, and of Demonstrator of Chemistry at Westminster Schools. He will now leave London to reside in Penzance, where he will commence work almost immediately.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 8, August 22, 1892.

Combustion-Heat of Various Chlorine Compounds.—MM. Berthelot and Matignon.

Glyoxylic or Dioxycetic Acid.—MM. Berthelot and Matignon.—These two thermo-chemical papers, whilst not admitting of useful abstraction, are not sufficiently important for insertion in full.

The Cholera: Its Causes and the Means of Preservation from It.—M. Pasteur, on presenting a recent work on this subject by Dr. Daremberg, called attention to the following points:—The author in one of the principal chapters of his book denounces emphatically the pollution of rivers by sewage, and equally the pollution of the soil by the distribution of sewage over the cultivated fields. He thinks that the germs of cholera, in the state of the exciting bacillus, may remain alive and virulent in the soil for several years, and may ultimately prove foci of cholera. The present cholera in the neighbourhood of Paris may be derived from the germs of cholera which have thus been preserved since the last epidemic of 1884. Dr. Daremberg, in the course of his work, cites experiments which have been recently made to protect domestic animals, and even man, from cholera.

Thermo-chemical Study of Certain Organic Bodies of Mixed Functions.—Leo Vignon.—The presence of the ketone group CO = distinctly annuls the basic functions in the base COR₂; the thioketonic group CS = allows these functions partially to subsist.

Determination of Peptone by Precipitation in the State of Mercury Peptonate.—L. A. Hallopeau.—The author's method is to precipitate the solution of peptone, free from other albumenoids, by a large excess of mercuric nitrate in a neutral or very slightly acid solution. The precipitate, which is white, flocculent, and voluminous, falls almost instantly to the bottom of the vessel. It is allowed to settle for eighteen to twenty-four hours until the supernatant liquid is limpid. The liquid and afterwards the precipitate are next poured upon a tared filter, which is washed with cold water until the washings are no longer precipitated by sulphuretted hydrogen. The increase of the weight of the filter, after desiccation at from 106° to 108°, represents the weight of the mercury peptonate; on multiplying this weight by the coefficient 0.666 we obtain that of the corresponding peptone. In order to determine this coefficient I precipitated with mercuric nitrate a known quantity of pure, dry peptone, prepared by the method of Henninger. I weighed the mercuric peptonate thus formed and calculated the proportion between the peptone used and the mercuric peptonate precipitated. I had previously ascertained by a combustion the purity of the peptone which served as an initial point. We may ascertain whether the precipitation with mercuric nitrate is complete by testing the filtrate for peptone by means of phosphomolybdic acid, which must not give a precipitate. The mercuric nitrate is purified from free nitric acid, which attacks the peptonate, by the following method:—100 or 150 grms. of pure mercuric nitrate are heated on the water-bath for fifteen to twenty minutes with 1 litre of water. The filtrate is heated almost to ebullition in a porcelain capsule. At this moment we add, whilst stirring, a few drops of solution of sodium carbonate until the precipitate of mercuric oxide formed ceases to re-dissolve. The liquid is filtered and diluted to 1 litre. The presence of chlorides does not interfere if a large excess of mercuric nitrate is used.

If the liquid in question contains other albumenoids they must be previously eliminated by the following process:—The liquid, if acid, is exactly neutralised with sodium carbonate when syntonine is precipitated. It is collected on a tared filter and washed with cold water. The increase of the weight of the filter (dried at 105°) shows the weight of syntonine. To the filtrate is added a drop of acetic acid, and it is heated for thirty minutes on the water-bath. Albumen is precipitated in flocks, which are collected on a tared filter and determined in the ordinary manner. To the filtrate we add nitric acid, drop by drop, until a turbidity is formed. The liquid is stirred for an instant, and the precipitate (hemi-albuminose) is allowed to settle. It is thrown upon a filter and washed with a little water containing a trace of nitric acid.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 6.

New Exsiccator.—W. Hempel places the hygroscopic agent (calcium chloride or sulphuric acid, &c.) above the substance to be dried. E. Biltz calls in question the utility of this arrangement, and W. Hempel replies.

An Extraction-Apparatus.—M. Karaz (*Zeit. Angew. Chemie*).—The principle of this device is essentially well known.

Cylinders with Overflow-Vessels.—R. Frühling and Jul. Schulz (*Zeit. Angew. Chemie*).—To prevent an overflow from cylinders used in taking the specific gravity of fluids by means of a hydrometer, the authors propose a concentric vessel surrounding the upper part of the cylinder.

New Determinations of the Specific Gravities of Hydrochloric Acids at Different Concentrations.—G. Lunge and L. Marchlewski (*Zeit. Angew. Chemie*).—A very complete set of tables.

Volumetric Determination of Tellurium.—B. Brauner.—This paper will be inserted in full.

Volumetric Determination of Sulphates.—H. Quantin.—From the *Bull. Soc. Chim. de Paris*.

Detection and Determination of Nitrous Acid.—P. F. Frankland.—From the *Journ. Chem. Soc.*

Detection of Alcohol in Varnishes, Pharmaceutical Preparations, &c.—Ad. Tscheppe (*Pharm. Rundschau and Chem. Zeit.*).—The author puts in a test-glass concentrated nitric acid (70 per cent), and pours above it the liquid in question. In presence of alcohol there appears a greenish colour, which in a few minutes passes into a brilliant deep emerald. Gradually there takes place a faint evolution of gas, and the characteristic odour of ethyl nitrite is recognised.

Detection of Cinnamic Acid.—T. L. Phipson.—From the *CHEMICAL NEWS*.

Detection of Resorcine.—L. Reuter (*Pharm. Zeit. and Chem. Zeit.*).—Already inserted.

Recognition of Furfurol.—E. Nickel (*Chem. Zeit.*).—Already inserted.

The Kjeldahl Process.—A. Atterberg (*Chem. Zeit.*).—The author has re-examined Gunning's modification of the original method, and finds that it yields correct results with such substances as the alkaloids, the azo-compounds, &c.

Determination of Glycerin.—J. Alfred Wanklyn and W. Johnstone.—From the *CHEMICAL NEWS*.

Rose's Method for the Determination of Alcohol.—Rud. Benedikt, also Leo Grünhut (*Chem. Zeit.*).—Both authors find the method untrustworthy.

Examination of the Sizing of Paper.—O. Schluttig and G. S. Neumann (*Papier Zeit.*).—The author founds his method on the permeability of the paper for solution of ferric chloride, applied upon one side of the sheet to be tested and solution of tannin applied on the other.

Detection of Naphthaline, α - and β -Naphthol.—L. Reuter (*Pharm. Zeit.* and *Chem. Zeit.*).—The author to discriminate between these three substances utilises the colour reactions which they give if heated for ten minutes with melted chloral hydrate. The colour reactions vary according as we use chloral hydrate alone, or, in addition, five drops of hydrochloric acid, or hydrochloric acid with zinc. The reactions are as follows:—

	0.1 grm. naphthalin.	0.1 grm. α -naphthol.	0.1 grm. β -naphthol.
With 2.5 grm. chloral hydrate.	less.	transparent, non-fluorescent.	Pure blue, transparent, non-fluorescent.
With 2.5 grm. chloral hydrate + HCl.	Almost colourless, very faint rose.	Intense greenish blue, opaque.	deep Intense yellow, transparent.
With chloral hydrate as before, + zinc.	Violet, then brownish.	Deep violet-blue, on adding water violet flocks which dissolve in alcohol with a reddish violet with violet fluorescence.	Deep dark brown; on adding water separation of a smeary substance which dissolves in alcohol with a yellow colour, with blue fluorescence.

Methods Proposed for determining Paratoluidine in Commercial Toluidines.—F. F. Raabe (*Chem. Zeit.*).—Already inserted.

Analysis of Milk.—A collection of extracts from a variety of journals for which we must refer to the original.

Recognition of Linen Fibre and its Distinction from Cotton Fibre.—M. Wiesner (*Dingler*).—The author applies chromic acid. Linen fibre after a few seconds appears as if cut up into transverse portions, whilst cotton fibre, if similarly treated, is split up as if into bristles.

Conditions of Calcium Carbonate in the Soil.—F. Reverdin and Ch. de la Harpe (*Chem. Zeit.*) propose a method for determining the assimilable lime in the soil. The method depends on the consideration that oxalic acid and the oxalates only attack the surfaces of the particles of calcium carbonate and convert them into calcium oxalate, whilst only these same surfaces are capable of assimilation by vegetation.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1714.

THE COLOURS AND ABSORPTION-SPECTRA OF THIN METALLIC FILMS AND OF INCANDESCENT VAPOURS OF THE METALS; WITH SOME OBSERVATIONS ON ELECTRICAL VOLATILITY.*

By WILLIAM L. DUDLEY.

SEVERAL years ago the writer began to investigate methods for obtaining metals in thin films, with a view to the study of the relations existing between their colour by transmitted light and that emitted by their incandescent vapours; also to the study of their absorption-spectra. A number of methods were resorted to; for instance:—

1. Volatilisation by boiling and condensation on glass;
2. Electro-deposition and removal of the "base" on which the metal is deposited by a suitable solvent;
3. Reduction of a salt which had been spread in a thin and uniform layer on the surface of a transparent base;
4. Volatilisation by the electric arc between terminals of the metal enclosed in a glass tube filled with an inert atmosphere; and
5. Volatilisation by the condensed electric spark under similar conditions.

Each method had its value in particular cases, but no one method seemed to be capable of universal application, although the last mentioned was generally applicable. I will describe briefly the various methods employed.

(1) Volatilisation by boiling was resorted to in dealing with potassium, sodium, and lithium. Potassium, which had been freed from all mechanical impurities and hydrocarbons, was introduced into a glass tube filled with an atmosphere of hydrogen or nitrogen which was highly attenuated by a pump, and sealed. The portion of the tube in which lay the globule of metal was gradually heated over a Bunsen burner until the potassium boiled, when the tube was immediately withdrawn from the flame. The vapour of the potassium condensed in a thin film on the cooler portions of the tube, and exhibited in the thinnest parts colours by transmitted light ranging from violet to blue as the thickness increased, while by reflected light the film had the usual silvery metallic lustre of potassium. The film is not permanent. The brilliant colours gradually fade, until after some days they have completely disappeared, owing to the thin layer slowly drawing itself together into minute globules which to the unaided eye give to the whole surface a frosted appearance. By again heating the metal to boiling as before a new film can be produced.

Sodium and lithium were treated in the same manner as potassium. Sodium, however, gave a yellow-brown film, which was due to its action on the glass; the colour was at first ascribed to the reduction of silica, but when lithium was treated in the same way the glass was also attacked, the colour of the film being deep red-brown. The glass was permanently coloured in each case, the metals having combined chemically with it, as one would naturally expect. The colour conveyed by each was, however, a source of surprise, since it approached more or less closely, even under these circumstances, to that of its incandescent vapour. It may be accounted for in the same way as is gold "ruby" glass, *i.e.*, is due to the presence of finely divided metal distributed through the glass. If thin gold leaf, which exhibits a fine green colour by transmitted light, be spread out on a sheet of glass and heated to 316° or over, the colour becomes red,

and if the temperature has not been so high as to incorporate the gold with the glass, the green colour may be restored by simply burnishing the surface (Faraday, *Phil. Trans.*, 1857, 145; also his "Experimental Researches in Chemistry and Physics"). The ruby colour of the glass is held to be due to the gold in a finely divided state, and the colours given to glass by sodium and lithium may be due to the same cause. Many kinds of glass were employed,—all, of course, without lead in their composition,—and the effect was always the same.

(2) Electro-deposition is of limited application; gold films may, however, be readily produced, owing to the ease with which this metal is deposited; its resistance, too, to the action of acids making the separation of the film from the metal upon which it is deposited a simple matter (Outerbridge, Paper by Eggleston, *Trans. Am. Inst. Min. Eng.*, vii., p. 91). A difficulty is encountered in this method in efforts to obtain films of proper thickness; this is, however, largely obviated by a method employed by Kundt ("Ueber die Brechungsexponenten der Metalle," *Ann. der Phys. Wied.*, xxxiv., 469), in which he obtains a wedge-shaped film by placing the cathode horizontal in the bath and the anode very near, and perpendicular to, the surface of the cathode. Thus the film tapers out in a very thin edge. Arsenic deposited on glass by decomposing arsine may prove a good surface upon which to make the deposits, as it could easily be dissolved off of the film by sodium hypochlorite or some other suitable solvent. I have never tried it, however, as I found that other methods served my purpose in most instances.

(3) The reduction of a thin film of the metallic salt was found unsatisfactory for various reasons, and was not employed, although films of platinum could be obtained quite easily, giving a purple colour by transmitted light.

(4) The electric arc between terminals of the metal to be volatilised proved successful in a few cases. The terminals were inserted into a glass tube filled with an inert atmosphere, and brought in contact for an instant. The metal was suddenly vapourised and thrown upon the glass, but was usually granular or powdery, of a black or brown colour, altogether unsatisfactory, owing to its discontinuous character.

(5) The condensed spark between two points of the metal enclosed in a glass tube, exhausted, or filled with an inert atmosphere highly attenuated, serves well in many cases. For descriptions of this method in detail I refer to papers by Wright ("On the Production of Transparent Films by the Electrical Discharge in Exhausted Tubes," *Amer. Journ. Sci.*, [3], xiii., 49; xiv., 169), Hartley ("On Films produced by Vapourised Metals and their Applications to Chemical Analysis," *Proc. Royal Society*, xlv., 88), and Crookes ("On Electrical Evaporation," *CHEMICAL NEWS*, lxiii., 287). Hartley, however, volatilised the metals in the air, and consequently only a few of the films were metallic. The facility with which metals volatilise by this method varies very much, those of low atomic weights showing, as a rule, more resistance than the heavier metals to the action of the spark. According to Crookes, this power of resistance does not increase regularly as the atomic weight decreases. No relationship has yet been discovered between the degree of electrical volatility and any known constant. Some relationship might be discovered if the volatilisation were carried on under such conditions of temperature and pressure as would most likely insure similar molecular conditions in each case. This might possibly involve the melting-point, as well as the atomic weight, as a factor.

If the order of the electrical volatility of the metals as found by Crookes be compared with Lothar Meyer's curve of atomic volumes, it will be found that the volatile metals lie at or near the minima of the curves, close together on the ascending sides in the periods IV., V., and VII., alternating from one to the other. Magnesium and aluminium, which are practically non-volatile, lie on the

* From the *American Chemical Journal*, vol. xiv., No. 3.

Metal.	Colour of Film.	Observer.	Colour of Incand. Vapour.	Observer.	Colour of Incand. Vapour as indicated by spectrum.
Gold	{ Pinkish, violet, blue, blue-green.	{ Faraday, Wright, and others.	Green.	Dudley	Green.
Heated to 316°..	Green.	Crookes and others.			
Heated on glass	{ Red. Red.	{ Faraday and Wright.			
Silver	Deep blue.	Wright.	{ Blue. Yellow-green in electric arc.	Stas. Dudley.	Yellow-green.
Copper	Green.	Wright, Fleming.	Green.	Dudley.	Green.
Aluminium	{ Fine blue. Brownish.	{ Fleming. Wright. }	Green-blue.	Dudley.	Green-blue.
Bismuth	Grey-blue.	Wright.	Blue, slightly greenish.	Dudley.	Blue-green.
Platinum	{ Blue-grey. Purple.	{ Wright. } Dudley. }	Blue (?)	Dudley.	Blue.
Palladium	Smoky brown.	Wright.	Green.	Deville and Debray (?)	Green.
Lead	{ Smoky brown, inclining toward olive.	Wright.	Blue.	Dudley.	Blue.
Zinc	{ Grey blue, less deep than Ag, deeper than Bi.	Wright.	Green-blue.	Dudley.	Green-blue.
Cadmium	{ Grey blue, about same as Zn, slightly less in- tense.	Wright.	Green.	Dudley.	Green.
Magnesium	{ Grey blue, similar to Zn and Cd, but less clear.	Wright.	Green.	Wright.	Green.
Tin	Brown-grey.	Wright.	Blue (?)	Dudley.	Blue-green (?)
Iron	{ Neutral tint with faint tinge of brown.	Wright.	Green-blue.	Dudley.	Green-blue.
Nickel	Grey or brown-grey.	Wright.	Blue-green.	Dudley.	Blue-green.
Cobalt	Grey or brown-grey.	Wright.	Green-blue.	Dudley.	Green-blue.
Tellurium	Dull purple.	Wright.	Golden yellow.	Gernez.	Orange-yellow.
Potassium	Blue-violet.	Dudley.	Violet.	Davy.	Violet.
Sodium heated on glass	Brown-yellow.	Dudley.	Yellow.	Davy.	Yellow.
Lithium heated on glass	Dark brown red.	Dudley.	Red.	Arfvedson (?)	Red.

descending side of period III. Aluminium, which is less difficult to volatilise than magnesium, is nearer the minimum of the curve. The metals given in the order of their electrical volatility alternate in the periods as follows:—

Metal.	Comparative electrical volatility.—Crookes.	Period.
Pd	108°	V.
Au	100°	VII.
Ag	82·68	V.
Pb	75·04	VII.
Sn	56·96	V.
Pt	44·00	VII.
Cu	40·24	IV.
Cd	31·99	V.
Ni	10·99	IV.
Ir	10·49	VII.
Fe	5·50	IV.

A thin, reguline, and coherent film of a metal transmits light of a colour remarkably similar to that emitted by its incandescent vapour. The colour of the vapour of a metal varies with the temperature. Just above its boiling-point the vapour of sodium is purple; at incandescence, yellow. The vapour of potassium is green; at incandescence, violet. Silver in distilling gives off a blue-white vapour, while that volatilised by the electric arc passing between silver electrodes emits yellowish-green light. The colour of the film obtained in many cases agrees very well with that of the incandescent vapour. In some instances, however, there is no similarity (see table above), a fact which is probably due to failure to obtain the proper conditions for the volatilisation and deposition. The perfection and continuity of the deposit is easily destroyed by very slight changes in the conditions. For instance, the aluminium film deposited by Wright by condensed sparks was brownish,

while that observed by Fleming (Discourse delivered at the Royal Institution, *The Electrician*, xxiv., 393), which resulted from the volatilisation of an aluminium connection in an overheated incandescent lamp, was of a "fine blue" colour in the thinnest portions.

The colour of the incandescent vapour of a metal is the resultant of the colours of the various rays emitted, and depends on the number and intensities of these rays; the colour can therefore be fairly predicted on examining a table of the wave-lengths and relative intensities of the spectral lines of the metal.

I give above a table containing a number of metals, in which is given the colour of the films by transmitted light, and the colour of the incandescent vapour as observed and as indicated from the spectral lines. The authorities are given as far as possible. In some cases I have been unable to find any mention of the colour of the incandescent vapour, although I am sure it must have been observed. In such cases I put my own name.

The colour of a film will vary somewhat with the thickness, but as far as I have observed the colours extend over a very limited portion of the spectrum. Each metal possesses a strong tendency toward a characteristic colour which is produced when the film is as thick as it can be to transmit any light.

Absorption-Spectra of Metallic Films.

Many of the films which corresponded closely in colour to the incandescent vapour of the respective metals were examined carefully as to their absorption spectra by throwing a powerful beam of white light through them. If the same molecular condition existed in the film as in the incandescent vapour we would expect to have the same absorption. In other words, the dark lines of the absorption spectrum of the film should coincide with the bright lines of the emission spectrum of the incandescent

vapour. I found in every case, however, that the films gave simply general absorption, no bands or lines being indicated.

THE SYNTHESIS OF SUGARS.

By W. E. STONE, Purdue University.

DURING the last five years there have appeared in the *Berichte der Deutschen Chemischen Gesellschaft* a series of remarkable papers presenting the details of the researches of Emil Fischer and his associates upon the synthetical production of sugars. These researches are of great theoretical interest from the light they cast upon the constitution of the sugars, as well as from the many new and important reactions which they have developed. As a whole this work may be classed among the notable achievements of the decade in organic chemistry. Aside from this, so much has been contributed to the stock of positive knowledge about this important group of compounds, that the results are of equal interest to the student of either theoretical or applied chemistry. In reviewing the work one cannot escape the impression that it is the beginning of many important results, both theoretical and practical, and that future research with these bodies must be largely prosecuted along the lines here laid down.

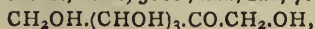
On account of the interrupted appearance of these papers it is thought that a comprehensive *resumé* of the same will bring the results into more accessible form, especially for those who do not read German with facility.*

To produce sugar synthetically has been one of the air castles of organic chemistry since the possibility of organic synthesis was established. Two great obstacles, however, have prevented the successful ending of many, more or less scientific, experiments in this direction. These were, first, ignorance of the chemical constitution of the sugars as explained by modern chemical theory; and second, the absence of successful methods for the separation and recognition of small quantities of sugars, especially in the presence of a large proportion of impurities, as well as of synthetical methods suited to the complex and unstable sugar molecule. Finally, the results obtained after these obstacles were overcome can only be understood and explained by the principles of the modern theories of chemistry, which ascribe to each chemical molecule a distinct geometrical structure, and explain the phenomena of isomerism upon the basis of the different geometrical arrangement of the atoms composing the molecule.

So late as 1886 the only sugars of the glucose or hexatomic group ($C_6H_{12}O_6$) which had been well studied and specifically characterised were *dextrose*, *levulose*, and *galactose*. As these represented the derivatives of other more complex sugars (sucrose, maltose, lactose, &c.), they stood as a fairly well-defined nucleus about which were clustered numerous other, more or less thoroughly studied, compounds. Of these sugars, dextrose and galactose had been shown to be normal pentoxy-aldehyds (*Berichte d. Deutschen Chem. Gesellschaft*), xxiii. 2115),—



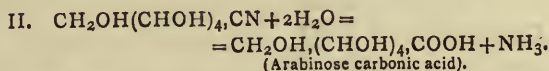
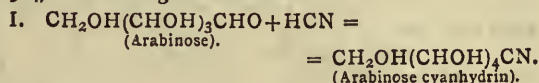
while levulose was regarded as a normal pentoxy-ketone (*Berichte D. Ch. G.*, xviii., 3066; xix., 221, 767, 1916),—



all three being regarded as theoretical derivatives of the normal hexatomic alcohol, $C_6H_{14}O_6$. These conclusions were arrived at from the behaviour of the given sugars toward oxidising and reducing agents. Another body, for many years classified with the glucose group, viz.,

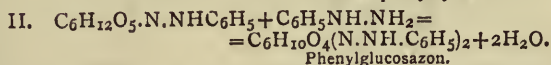
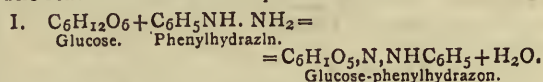
arabinose, was found in 1887 to be a normal tetroxy-aldehyd, $CH_2OH.(CHOH)_3.CHO$, corresponding to the pentatomic alcohol, $C_5H_{12}O_5$ (*Berichte D. Ch. G.*, xx., 339). Definite knowledge of the constitution of these four sugars was the first important step toward their synthesis, showing as it did their relation to other carbon compounds. But this theoretical knowledge alone would never have sufficed to accomplish even the beginning of the extraordinary syntheses which are to be credited to Fischer. They were only possible by the aid of certain reactions and methods, most of which have also originated with the same investigator.

The first of these reactions, however, we owe to H. Kiliani, who showed that hydrocyanic acid could be added to an aldehyd or ketone sugar, forming a cyanhydrin, which on being heated with a basic oxide (baryta) becomes saponified, producing a monobasic oxy-acid with one more carbon atoms than the sugar employed (*Berichte D. Ch. G.* xviii., 3066; xix., 221, 767, 1128, 1914). Following is the reaction:—



This typical reaction is the same by which Kiliani proved the constitution of arabinose, and has since been made of use of by Fischer for the synthetical step from a lower to a higher group of sugars, as for instance from $C_6H_{12}O_6$ to $C_7H_{14}O_7$.

A more general reaction than this is that discovered by Fischer between aldehyds or ketones and phenylhydrazin (*Berichte D. Ch. G.*, xvii., 572), and first applied by him for the characterisation of sugars (*Berichte D. Ch. G.*, xvii., 579). The reaction occurs readily with all aldehyd or ketone sugars forming characteristic crystalline, insoluble compounds. The method is as follows:—A 10 per cent watery solution of the sugar receives an acetic acid solution of phenylhydrazin, and, on heating the mixture in a water-bath at 75° to 85°, there soon begins a precipitation of fine yellow crystals of the composition $C_{18}H_{22}N_4O_4$ (if the sugar be of the $C_6H_{12}O_6$ group). The reaction occurs in two phases as follows:—



The first product is, in nearly all cases, soluble in water, but, on heating, the "osazon," containing a second molecule of phenylhydrazin, is precipitated. The "osazon" thus produced from all of the sugars which reduce Fehling's solution are stable bodies, easily separated from accompanying impurities, easily purified and serving to characterise—either by analysis or melting-point—the sugars from which they are derived. The melting-points of the "osazons" of the well-known sugars illustrate this:—

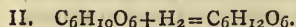
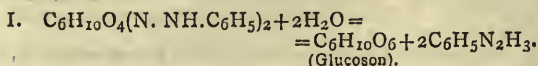
Glucosazon, 205°	Maltosazon, 206°
Galactosazon, 193°	Rhamnosazon, 180°
Sorbinosazon, 164°	Arabinosazon, 560°
Lactosazon, 200°	Xylosazon, 160°.

This reaction is safely the most important means yet discovered for separating and identifying small quantities of sugars in the presence of impurities or foreign bodies.

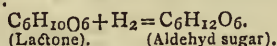
Fischer has also succeeded in regaining the sugar from its osazon, and the latter has thus served in several cases as a means for isolating a newly prepared sugar, yielding

* Fischer himself has reviewed a portion of this work before the German Chemical Society, in June, 1890. See *Berichte*, xxiii., 2114. The work previous to 1890 has also been reviewed by Dr. E. H. Keiser in *American Chemical Journal*, xi., p. 277; and xii., p. 357.

it up again in a pure form. This result is obtained by treating the osazon with fuming hydrochloric acid, by which the phenylhydrazin is split off, leaving a body called an "oson," which by reduction becomes the sugar (*Berichte D. Ch. G.*, xxii., 87). Following is the reaction:—



A third reaction, which has played a very important part in these syntheses is the method devised by Fischer for the reduction of the acids of the sugar group to their corresponding aldehyds (*Berichte D. Ch. G.*, xxii., 2204). This reaction does not occur with the free acids; but Kiliani has shown that the oxy-acids of the sugar series easily form lactones by loss of water, on evaporation of their watery solutions. Such lactones were found by Fischer to be readily reduced to corresponding aldehyds (sugars) by the action of sodium amalgam upon their watery solution.



This reaction occurs, however, only in an acid solution, i. e., when small quantities of sulphuric acid are added successively to the solutions in which the reduction is taking place.

It will be seen that this reaction, in connection with the addition of hydrocyanic acid to an aldehyd sugar, as already described, supplies all the steps for the synthesis of one sugar from another containing one less carbon atom, the compounds being derived from each other in this order:—Arabinose ($\text{C}_5\text{H}_{10}\text{O}_5$), arabinose-cyanhydrin, arabinose-carbonic acid, the lactone of this acid, and finally the glucose with six carbon atoms ($\text{C}_6\text{H}_{12}\text{O}_6$).

Several other new reactions, of quite equal importance to the success of these researches will be described later, but these suffice to introduce the work of Fischer and his collaborators.

It having been established that the glucoses possessed the structure of aldehyds or ketones, there naturally followed attempts to produce the same by a mild oxidation of the corresponding hexatomic alcohols. All the earlier attempts to carry out this reaction led, however, to no definite results, although the products thus obtained from mannitol and dulcitol exhibited some of the properties of the sugars (fermentability and reducing action upon Fehling's solution). Fischer repeated this oxidation, and, by means of the phenylhydrazin, isolated the sugar thus obtained, found that it had the same structure as grape sugar (a pentoxy-aldehyd), and ascertained that the latter was not the true aldehyd of mannitol, as had been supposed, but that it belonged to a different series of stereoisomeric compounds (*Berichte D. Ch. G.*, xxii., 374). The sugar obtained from mannitol was called mannose, and has since been obtained by hydrolysis from various natural materials (Tollens and Gans, *Annalen Chem. u. Pharm.*, cclxvi., 256; Reiss, *Berichte*, xxii., 609, 3218).

In a similar manner has been obtained from the tetra-atomic alcohol erythrit a sugar called erythrose, and from the triatomic alcohol glycerin a sugar named glycerose (*Berichte D. Ch. G.*, xxii., 1088).

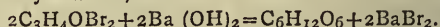
All this was far removed from the actual synthesis of sugars, and the experimenter was at this time far from seeing his way through the different steps, now so well defined.

The way to the actual building up of the sugar molecule had been suggested by different workers before Fischer finally succeeded. Butlerow's methylenitan (*Annalen Chem. u. Pharm.*, cxx., 295), obtained from formaldehyd, a sweet, reducing, but not fermentable and optically inactive syrup, is regarded by Fischer as the beginning of this matter; and indeed this was used by Baeyer as the basis of his theory for the formation of

sugar in the plant, viz., the polymerisation of formaldehyd. Later, Tollens made a similar observation, upon treating formaldehyd with lime-water,* and, following him, Loew studied the product to which was given the name *formose* (*Ann. Prakt. Chemie* [2], xxxiii., 321).

In none of these cases was the product well characterized or isolated. In Fischer's hands, however, the formaldehyd derivative was shown to be a mixture of various sugar-like bodies, of which one—non-fermentable and optically inactive—still retains the name *formose* (*Berichte D. Ch. G.*, xxi., 989).

Meantime came a most important discovery by Fischer (*Berichte D. Ch. G.*, xx., 1093, 2566), viz., that a sugar-like body was produced by treating acrolein bibromide with baryta-water,—



From the products of this reaction were isolated by means of phenylhydrazin two isomeric sugar-like bodies called respectively α - and β -acrose.

Identical with the above were products obtained by treating glycerose with a weak alkali (*Berichte D. Ch. G.*, xx., 3384). This latter attainment is of physiological interest because secured under mild conditions, possible in living organisms.

Of these synthetic products the α -acrose was the most important. This was now found to be identical with one of the bodies resulting in small quantities along with *formose*, from the polymerisation of formaldehyd (*loc. cit.*). This α -acrose was separated from other reaction products by means of phenylhydrazin as the α -acrosazon, which, by the method already referred to, yielded α -acrosone, and this again, by reduction, a sweet syrup which reduced Fehling's solution, fermented with yeast, yielded levulinic acid on treatment with hydrochloric acid, and, in short, gave all the reaction of the glucoses, but was *optically inactive*. By means of sodium amalgam it was reduced to a hexatomic alcohol (α -acrit), which closely resembled mannitol, save that it was also *optically inactive* (*Berichte D. Ch. G.*, xxii., 97). This optical property was at that time impossible to explain, but has since been found to characterise an altogether new and numerous series of synthetic sugars.

The α -acrose was regarded as a true sugar, and being derived from formaldehyd (or glycerose) as described, the synthesis of a member of the sugar group may be regarded as complete at this stage, although there still remained a gap between the artificial sugar and any natural one. To accomplish so much, however, had required great patience and skill, involving the treatment of large amounts of materials, while the ultimate products were obtained in such small quantities as to preclude their close study. The synthesis of sugars would never have reached anything like its present stage if dependent on the operations thus far described.

(To be continued.)

PIPETTES FOR MEASURING POISONOUS LIQUIDS.

By ALEX. F. REID, of Bonshaw, Stewarton, N.B.

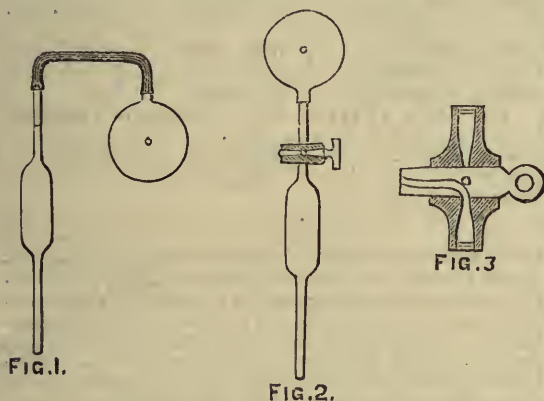
In my last contribution (*CHEMICAL NEWS*, lxxv., p. 125) I described some improvements upon burettes. I will now describe two improved pipettes for measuring the poisonous liquids.

In measuring poisonous liquids with a pipette it is usual to put a piece of cotton-wool or other like material, moistened with an antidote, in the top of the tube of the

* *Berichte D. Ch. G.*, xv., 1629. Since this, Tollens and Wiegand have shown that a mixture of formaldehyd and acetaldehyd with lime-water, on standing three to four months, polymerised to form penta-erythrit, $\text{C}(\text{CH}_2\text{OH})_4$. *Annalen Chem. u. Pharm.*, cclxv., 316.

Pipette. In the pipettes I am going to describe this precaution is obviated.

Fig. 1 is a common pipette with about 6 inches of india-rubber tube attached to the upper end of it. To this india-rubber tube is attached an india-rubber ball by means of a short piece of glass tube. This india-rubber ball has a hole in its side. To fill the pipette with liquid the moistened thumb of the right hand is placed upon the orifice of the ball, and the latter compressed. The point of the pipette is now put into the liquid, and the ball slowly allowed to regain its normal dimensions, still keeping the thumb on the hole. The liquid rises in the pipette, and when it comes to the mark the india-rubber tube is clipped by the thumb and finger of the other hand. The thumb is now taken away from the hole in the ball,



then the thumb and finger from the india-rubber tube, and the liquid allowed to run out. After some practice this can be done as easily as—in fact more easily than—with the mouth, as you can more readily see what you are doing.

Fig. 2 is a form of pipette in which the india-rubber ball may be attached directly to the top of the pipette, and in which it is not necessary to always fill the pipette to the same mark, a three-way stopcock being in the place where the mark would otherwise be. The liquid is drawn up by the compressed ball into the upper part of the tube, and the stopcock slightly turned. By turning it further, into the position shown in Fig. 3, the measured liquid runs out of the pipette.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, September 12th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 2nd to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and

Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

As will be seen from the Tables, the water-supply to the Metropolis during the month of August continued to be of excellent quality, the proportions of organic matter present, estimated alike by the combustion and oxygen processes, and by the degree of colour-tint, being, as now for some months past, extremely small. In the case of the Thames-derived supplies, for example, the mean proportion of organic carbon amounted to 0.015 part in 100,000 parts of the water, this being 0.002 part in excess of the mean for June, and 0.020 part in excess of the mean for July, minute differences of no practical significance. The maximum proportion of organic matter present in any single sample examined was found to be identical with that of the previous month, or 0.152 part in 100,000 parts, corresponding roughly to about a quarter of a grain of organic matter per gallon. The amount of organic matter found in the water furnished by the Chelsea Company was again exceptionally low, the mean proportion of organic carbon in that Company's supply and in the supply of the New River Company, or 0.078 and 0.079 part in 100,000 respectively, being to all intents identical.

From time to time, in periods of flood or after violent rainfall, we find in the course of our examinations of the daily supply furnished by the different companies, an occasional sample which, when viewed in bulk, exhibits a distinct turbidity; and from some cause or another, one such instance was met with among the 175 samples examined last month. More often, but still only occasionally, samples are met with manifesting on careful examination through a depth of two feet, a slight deficiency in brightness. These samples we have been accustomed all along to indicate by the letters V.S.T., standing for "very slightly turbid," an expression, however, suggesting somewhat more than is warranted, since under common observation these samples would be regarded as perfectly clear.

The effect of any ordinary excess of rainfall is, as doubtless with an increase of storage capacity that of an extraordinary excess would be, almost inappreciable. During the past month the rainfall at Oxford was 1.38 inch above the average; and of the entire 3.62 inches of fall, 1.02 inch was contributed on a single day, and over half an inch on each of two other days with only one intervening day between them. Yet in the entire month's supply furnished by three out of the five Thames Companies, not a single sample having even to be indicated by the letters V.S.T. was met with.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.

CHEMICAL EXAMINATION OF HAND-WRITING.

By A. ROBERTSON and J. HOFMANN.

THE authors draw lines across the letters or figures with quill pens dipped in the following reagents, and observe the changes where the ink and the reagent meet, using, if needful, a magnifying power of 100 diameters. The reagents are:—(1) A 3 per cent solution of oxalic acid; (2) a 10 per cent solution of tartaric acid; (3) a 2 per cent solution of chloride of lime; (4) solution of 1 part stannous chloride in 1 part hydrochloric acid and 10 parts

Reagents.	Iron and gall ink.	Logwood with—		Nigrosine.	Vanadium ink.	Resorcin ink.
		Potassium chromate.	Copper sulphate.			
Oxalic acid	Disappears.	Violet.	Orange.	No change.	Turns pale and runs a little.	Bright red.
Citric acid	Turns pale.	Violet.	Orange.	Runs dark blue.	Turns pale and runs.	Disappears.
HCl.. .. .	Disappears, but leaves a yellow.	Purple red.	Blood red.	Little change.	Slightly paler and runs slightly.	Light rose.
Sulphuric acid ..	Disappears.	Red.	Purple red.	No change.	Slightly paler.	Bright red.
Nitric acid	Disappears.	Red.	Purple red.	Runs slightly.	Slightly paler.	Light rose.
Stannous chloride..	Disappears.	Red.	Magenta.	No change.	Slightly paler.	Disappears.
Sulphurous acid ..	Turns pale.	Violet grey.	Red.	No change.	Slightly paler and runs.	Turns paler.
Gold chloride.. .	Slightly paler.	Red-brown.	Brown.	No change.	No change.	Runs brown.
Sodium thiosulphate and NH ₃	Dark red.	No change.	Dark blue.	Dark violet, runs.	Runs much.	Brown.
Ferrocyanide and HCl	Blue.	Red.	Brick-red.	No change.	No change.	Rose.
Sodium hydroxide..	Dark red.	Brown.	Dark red, runs.	Dark violet, runs.	Dirty brown, runs.	No change.
Chloride of lime ..	Disappears.	Disappears.	Disappears leaving a yellow stain.	Brown.	No change.	Brown.

of water; (5) sulphuric acid at 15 per cent; (6) hydrochloric acid at 10 per cent; (7) nitric acid at 20 per cent; (8) saturated solution of sulphur dioxide; (9) 4 per cent solution of gold chloride; (10) solution of 1 part potassium ferrocyanide in 1 part hydrochloric acid and 10 parts water; (11) solution of 1 part sodium thiosulphate (hyposulphite) in 1 part ammonia and 10 parts water; (12) 4 per cent soda-lye.

The subjoined Table shows the results. The results with tartaric acid are not tabulated.—*Chemiker Zeitung*.

THE INFLUENCE OF THE CARBOXYL GROUP ON THE POISONOUS ACTION OF THE AROMATIC COMPOUNDS.

By W. NENCKI and H. BAUTMY.

THE researches of the authors are intended to show, on the basis of earlier as well as recent facts, that the introduction of the carboxyl group, CO₂H, into the molecule of a great number of aromatic compounds involves a great decrease of their toxic action.

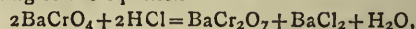
As the main cause of poisoning is to be sought in reductive phenomena, the diminution of the toxic action may be explained by the consideration that it represents a group saturated with oxygen which is not further reduced in the organism. Benzol, naphthaline, pyridine, quinoline, are well known to be rather powerful poisons. Benzol- and naphthaline carbonic acids are feeble poisons, and such will be found to be the corresponding carboxyl-compounds of quinoline and pyridine. Whilst the phenols exert a powerfully toxic action this is considerably lessened in the corresponding carbon acids. Carboxyl, however, diminishes the toxic power not only in the aromatic hydrocarbons, amines, and phenols, but also in very complex aromatic compounds. Antifibrine (?) is eliminated in the urine as orthoxycarbonil, the sulpho-salt of which possesses, according to Demme, a considerably poisonous action. The corresponding orthoxyl-carbonil-carbonic acid,—a white crystalline substance, fusible at 300°, and very sparingly soluble in the ordinary solvents, has no poisonous effect upon dogs even in daily doses of 5 grms. Malonanilic acid, which may be regarded as an acetanilide in which a hydroxyl of the methyl-group is replaced by carboxyl, melts at 135°; it crystallises in transparent laminæ, and is readily soluble in

ether, alcohol, and water. The sodium salt of malonanilic acid has been found perfectly inactive in febrile affections. Paraphenacetine-carbonic acid, a phenacetine substituted with carboxyl, melts at 134°, crystallises in rhombic needles, is readily soluble in alcohol, but sparingly in water. Whilst phenacetine exerts well-known characteristic effects, capable of therapeutic utilisation, phenacetine-carbonic acid is perfectly inert.—*Archiv. de Science Biologique de St. Petersburg* and *Chemiker Zeitung*.

ON THE VOLUMETRIC DETERMINATION OF SULPHURIC ACID IN SULPHATES.

By PROF. A. VON ASBOTH.

E. STOLLE recently proposed in the *Chemiker Zeitung* a method for the volumetric determination of sulphuric acid. Barium chromate dissolves in hydrochloric acid according to the equation—



and from this solution ammonia precipitates all the chromic acid as neutral barium chromate.

A hydrochloric solution of barium chromate is used for the precipitation of the sulphuric acid; there is thrown down on supersaturation with ammonia a quantity of barium chromate corresponding to the barium still remaining in solution, whilst the residue of the chromic acid remains dissolved. This chromic acid, still in solution, is titrated after acidulation by sulphuric acid with a solution of ferrous oxide, using potassium ferricyanide as indicator. This chromic acid is the direct measure for the sulphuric acid present.

Prof. von Asboth being in want of a rapid method for the determination of sulphuric acid tested this process at once. The solution of barium chromate was prepared as directed, particular care being taken that neither barium chloride nor potassium chromate remained in solution. For the analysis he used chemically pure potassium sulphate. The first analysis was executed 24 hours after the preparation of the solution of barium chromate. The author obtained 87.00 per cent K₂SO₄; in the afternoon of the same day he found 86.80 per cent K₂SO₄, and five days afterwards the method indicated only 55.10 per cent of K₂SO₄.

The solution of barium chromate in the bottle, after standing for some time, gave off a strong smell of chlo-

rine. This odour gave at once the explanation. A part of the chromic acid, or we may say of the barium bichromate, passes into decomposition in contact with hydrochloric acid, with the formation of chlorine and probably chromium chloride along with the barium chromate. As a part of the chromic acid is already decomposed on supersaturation with ammonia, there remains barium chloride in solution. This barium chloride eliminates one part of the sulphuric acid, and as we calculate the quantity of sulphuric acid from the chromic acid which has passed into solution, it is plain that we always obtain less sulphuric acid than is actually present. The longer the solution of barium chromate is kept the more chromic acid is decomposed and the less sulphuric acid will be found. As a proof that these suppositions are correct the author has prepared neutral barium chromate, and washed the precipitate until the filtrate no longer gave the reactions for barium chloride. The precipitate was dissolved in dilute hydrochloric acid and set aside for 24 hours. After the supersaturation a part of the solution was treated with ammonia and barium chloride was found in the filtrate.

From these experiments it follows that Stolle's method is not available for the volumetric determination of sulphuric acid. Perhaps neutral barium chromate might be kept in store in a moist condition, and the solution of barium chromate might be prepared afresh for every analysis. The decomposition would then not occur.—*Chemiker Zeitung*.

DETECTION AND DETERMINATION OF METALLIC LEAD AND LEAD COMPOUNDS IN COMMERCIAL TARTARIC AND CITRIC ACIDS.

By M. BUCKET.

BOTH the tartaric acid and the citric acid of commerce are often contaminated with metallic lead and compounds of this metal due to their preparation in leaden vessels. For the determination of the metallic lead we dissolve 200 grms. of the acid in question in three times its weight of water, and add ammonia in slight excess, so as to effect the perfect solution of any crystalline lead sulphate which may be present. After the lapse of 24 hours the liquid is decanted off and set aside; the precipitate formed is collected on a filter, carefully washed, and dissolved on the filter with nitric acid.

The nitric solution is concentrated and mixed first with sulphuric acid, and then with twice its volume of alcohol. The precipitate of lead sulphate is washed with alcohol, dried, ignited, and weighed. The solution of ammonium citrate (or tartrate) first obtained serves for the determination of the compounds of lead; the solution is acidulated with hydrochloric acid, precipitated with sulphuretted hydrogen water, and determined as lead sulphate as above.—*Repert. Pharmac. and Chemiker Zeitung*.

DETERMINATION OF SULPHUR IN FUELS BY ESCHKA'S PROCESS.

By DR. FRANZ HUNDESHAGEN.

THE method of Eschka, much recommended for the determination of sulphur in coal and other solid combustibles, consists in burning the substance in presence of sodium carbonate and magnesium oxide. The author recognises that a serious error may manifest itself in the application of this process, in consequence of the production of gaseous sulphur-compounds which escape condensation by the reagents employed. This loss, which may reach 6 per cent and more of the total sulphur, is essentially

due to a formation of sulphuretted hydrogen. It is easy to ascertain this by placing at the mouth of the crucible a paper moistened with a solution of lead.

We may escape this loss entirely, or almost entirely, by substituting in Eschka's mixture potassium carbonate for sodium carbonate. Hundeshagen finds that a mixture of one part dry potassium carbonate with two parts by weight of magnesium oxide is most advantageous in all places.

If we increase the proportion of potassa the mass becomes fritted at a red heat and the combustion of the coal is impeded. To one part of coal we use at least two parts of the above mixture; three-fourths of the reagent are intimately mixed with the finely-powdered coal, and the remaining one-fourth is spread at the top. The combustion proceeds more rapidly than with the soda mixture, and is generally completed in from a quarter to half an hour.

The inconvenience of Eschka's mixture is due in the first place to the property of sodium carbonate to become completely dehydrated at a low temperature, and to possess in this state only a very feeble power of absorbing sulphuretted hydrogen, &c.; and further, sodium sulphide is easily decomposed by moist carbonic anhydride.

The advantages of potassium carbonate lie in its power of fixing water even at a rather high temperature, and to react with sulphuretted hydrogen to form potassium hydrosulphate with an escape of carbonic anhydride.

This absorption of sulphuretted hydrogen is promoted by the fact that potassium carbonate, intimately mixed with magnesia, reacts partially with it under the action of watery vapour to form potassium hydroxide, the absorbent capacity of which for sulphur compounds is much superior to that of the carbonate. Sodium carbonate does not possess this property, or at least only in a very slight degree.

We may easily demonstrate the difference of action of the two alkaline carbonates with sulphuretted hydrogen. Sodium carbonate mixed intimately with a slight proportion of sodium sulphide and bicarbonate, or with ammonium sulphide, gives off a considerable quantity of sulphuretted hydrogen, especially if exposed to heat, whilst a very small addition of potassium carbonate, if intimately incorporated with the other ingredients, completely hinders this escape.—*Chemiker Zeitung*.

NOTICES OF BOOKS.

The Analytical Chemistry of the Fatty Substances. (Chimie Analytique du Matières Grasses.) Methods for the Assay and the Analysis of Oils, Tallow, Greases, Glycerines, "Turning" Oils, Butters, Waxes, Resins, &c. Examples of Analysis—Reports. By M. FERDINAND JEAN, Director of the Laboratory of the Commercial Exchange, Chief of the Laboratory of the French Society of Hygiene. Paris: Edmond Rousset et Cie. 1892. Large 8vo., pp. 636.

This elaborate work is founded upon a former publication of the author and M. Dalican, on the chemical methods used for determining the commercial value of oils and fats. Subsequently the author has devoted much attention to the examination of new methods for the analysis of these substances. In so doing he has utilised the exceptional facilities afforded by his official positions, and has studied critically the principal works on the subject which have latterly appeared. The result has been the present excellent volume.

The author confines himself to practical data concerning the assay and analysis—how does he draw a boundary line between these operations?—whilst leaving untouched the extraction and purification of the substances in question. He is fully sensible of the difficulty of the

subject. He declares that "all the science of the sophisticator consists in producing mixtures which with Lefebvre's oleometer present the specific gravity of pure oils." This, he tells us, is the sole means of control employed, even by the Commission on Oils of the Chamber of Commerce. At present it is rare for an absolutely pure oil to be obtainable in open market. Consequently their true characteristic properties can be determined only by chemists who possess exceptional opportunities. The colour-tests he rightly considers uncertain and variable. He might have added that often the reactions are due not to the oil itself, but to natural impurities which may or may not be present.

Among the physical properties of oils he lays the chief weight on the specific gravity, the thermic degree (Maumené's process), and the optical deviation. These three determinations are sufficient in a majority of cases to ascertain the purity or impurity of an oil. These tests are reinforced by a variety of other methods. According to MM. Doumer and Thibaut, a study of the absorption spectra of oils enables us to divide them into four categories. These authors experimented on expressed oils prepared at temperatures not exceeding 60°, the strata examined having been 12 m.m. in thickness.

The first class has the spectrum of chlorophyll. It includes the oils of olive, nuts, and hemp-seed. The spectrum of nut-oil has little luminosity, but the blue and violet bands are distinct.

The oils of sweet and bitter almonds and castor-oil have no spectrum.

On the contrary, colza, rape, linseed, and mustard oils absorb all the chemical radiations. The spectrum, instead of extending towards the blue, indigo, and violet, and gradually fading, ceases abruptly in the middle of the green.

The last category includes the oils of sesame, earth-nut poppy, colza, and cotton-seed, as characterised by three bands in "the chemical portion of the spectrum. It displays neither the green, orange, nor red bands characteristic of chlorophyll.

Among the physical methods described we find the determination of the electro-conductivity of oils (Rousseau's diagometer), and the oleographic method of Tomlinson and Moffat, which latter is described in full.

The optical analysis by means of the oleo-refractometer of E. H. Amagat and the author is described *in extenso*, with the useful addition of a table showing the deviations of the principal oils, crude and purified, and of sophisticated samples.

The Maumené process, as effected with the aid of the thermolæometer and with the improvement suggested by Ellis, is fully appreciated.

The determination of the chemical characteristics of the fatty bodies forms the subject of the third chapter. Here we find an account of the saponification number (Kœttstorfer's test), Hehner's number, Reichart-Meissl-Wolly's number; the iodine number (Hübl's), the bromine number, the acetyl and the nitril numbers.

The colour reactions are not omitted, though the author's confidence in them is not unlimited.

As an instance showing how thoroughly the characteristics of the several oils are described, we take one of them at random—earth-nut oil. Firstly come its synonyms, in French, Latin (for the benefit of the pharmacists), German, and English. Then follow its specific gravity at 15° correction for temperature; degree of the oleo-refractometer; Maumené's degree; congelation-point; specific gravity of the fatty acids at 100°; fusion and solidification-points of the fatty acids; iodine number; Hehner's number; bromine number; number of saponification, and acetyl number.

The detection of the sophistications of olive oil has been worked out with especial care.

The section on the Turkey-red oils, natural and artificial, is very satisfactory.

Our opinion of this work as a whole is extremely

favourable. It will prove of the highest utility to chemists engaged in any of the industries which make use of fatty matters and their products. We cannot, however, help noticing as a defect the want of an index. We regret, also, that the author has not seen his way to dispense with the vexatious hydrometric scale of Baumé.

Papers and Proceedings of the Royal Society of Tasmania for 1891. Hobart: Mercury Office.

WE have on former occasions noticed, with a feeling of regret, that our colonial brothers, at the meetings of their scientific gatherings, occupy themselves too much with matters which might be as conveniently—to say the least—discussed in Europe, leaving untouched questions which can be dealt with only under the Southern Cross. Very much of the Report before us consists of matter of the former class. Not a single chemical paper seems to have been read before the Society.

Force and Mass. Formers of the Cosmos. Identity of the Material Forces. ("Kraft und Masse. Bildner des Kosmos. Identität der Naturkräfte.") By RUDOLF MEWES. Part I. Berlin: Klein and Co. 1892.

THIS pamphlet by its title at once reminds us of the celebrated "Kraft und Stoff" of Büchner,—a happier name had it not been pre-engaged.

The author commences with a long and decidedly polemical preface. Herr Mewes remarks that the heads of the great publishing houses, before accepting a scientific work, take the opinion of the University professors, who do not feel themselves in a position to recommend books not drawn up from their own point of view. Hence the most "epoch-making" works are liable to be rejected, and owe their appearance to some fortunate accident. If we may venture to make a suggestion to *savants* who have not yet become popular, but who have—or believe that they have—arrived at some novel and important generalisation, we should advise them in drawing up a memoir or a pamphlet to place their theory or their generalisation by itself in the plainest language and in the fewest possible words, either at the beginning or the end of their work. It should be given in such a manner that "he who runs may read." Above all things it should be disentangled alike from metaphysical speculation and from mathematical formulæ. Having thus stated, *totidem verbis*, what they seek to prove, they should proceed to its demonstration and its illustration in such manner as they think most suitable.

Herr Mewes, in this the first part of his treatise, discusses the absorption and emission of the vibrations of the ether, the radiation of the waves of the ether, and the propagation of the ether waves of conduction. It is possible that in his second part he may proceed to answer the questions which his readers will long to put.

Concerning thermo-chemistry he declares that in its present form it has effected no essential advance for the principles of theoretical physics. "It is still involved in the old representations, and in the manner of the chemists of the old school it regards chemical processes as the effects of chemical affinity."

We look forward with interest to the second portion of this treatise, in which the author's conclusions may be expected to assume a crystalline form.

Chemical Theory for Beginners. By LEONARD DOBBIN, Ph.D., and JAMES WALKER, Ph.D., D.Sc., Assistants in the Chemistry Department, University of Edinburgh. London: Macmillan and Co., 1892. Small 8vo., pp. 236.

THE authors of this little work point out that the principles of chemistry—as compared with isolated facts—are too generally neglected in text-books, whether of smaller or larger dimensions. From the use of the smaller

manuals the student seldom obtains any satisfactory grasp of chemical theory, whilst in the more advanced treatises "the same subjects not unfrequently receive similar scant attention, because the student is supposed to have been introduced to them already." This complaint is not entirely unfounded. We can therefore express our satisfaction with the attempt made by Drs. Dobbin and Walker to set forth facts in combination with the theories to which they have led.

There is another feature in this work which deserves, we think, favourable consideration,—the entirely non-mathematical treatment of the more important principles of general chemistry. It is admitted that not a few important conclusions could never have been reached without the aid of the higher mathematics. But we submit that the results when thus reached may be expounded and dealt with in the absence of such methods. It would be vain to attempt to erect a cathedral or a palace without the intervention of scaffolding and ladders. But when the structure or any portion of it is completed, these auxiliaries are removed before it is thrown open to the inspection of the public.

We make these remarks because it is an error to assume that every man capable of doing service in Science must necessarily be a mathematician, or be capable of being trained to use mathematical methods. We therefore trust that the experiment of the authors may prove successful.

Agricultural Chemistry. A Familiar Explanation of the Chemical Principles Involved in the Operations of the Farm. By ALFRED SIBSON, F.C.S., Analytical and Consulting Chemist. With a Preface by the late Dr. AUGUST VOELCKER, Consulting Chemist to the Royal Agricultural Society. Revised, extended, and brought up to date by the AUTHOR and A. E. SIBSON, F.C.S. London, Manchester, and New York: G. Routledge and Sons, Limited, 1892. 8vo., pp. 348.

THE first edition of this book has long been favourably known to farmers. The present issue has been enriched with novel matter, especially on reverted phosphates, slag phosphates, sewage manures, ensilage, &c. On these subjects the views of the authors will not always be accepted without question. The Messrs. Sibson evidently set a higher value upon farmyard manure than is done by M. Ville and his school. They advance the opinion that farmyard manure is "the most economical source on which the farmer must rely for sustaining the fertility of his land," and that it is "the most complete, most valuable, and only perfect manure," and that "this substance only can return to the ground all the materials removed by cultivation." These, to say the least, are very strong statements. But farmyard manure contains at the least 90 per cent of matter which is useless, or which is fully supplied by the atmosphere and the rain, all which involves labour in conveying to the fields and spreading. If the soil is poor in any of the chief constituents of plant food, the farmyard manure obtained from its produce will obviously be deficient in that constituent, and will not improve land of the same quality.

Upon sewage manures the authors are disposed to be severe. On due inquiry they would find that sewage manure can be dried down to 14 or 15 per cent of moisture without the injurious addition of lime, and that it contains without any "fortification" 3 per cent of ammonia and 5 per cent of phosphate. Such a sewage manure is certainly far richer than farmyard manure. Of course the process now perpetrated in London of first precipitating the sewage and then carrying it out to sea is utterly deplorable, and fully justifies Messrs. Sibson's remark about the expenditure of millions to get rid of it. Almost equally to be condemned is the scheme here called "ingenious," of burning the sewage sludge, for converting it into cement. The sludge is mixed up with the materials necessary for producing cement and burnt.

But it adds nothing to the valuable properties of the cement, and all the manurial constituents are simply wasted just as much as if they had been turned into the sea.

Sewage-irrigation is of course an excellent expedient in climates such as South Africa, Australia, many parts of India, &c., where the rain-fall is either scanty or very intermittent. But in so cold and drizzly a region as England the case is very different.

It is very questionable whether in wet seasons the "Gillwell harvest saver" is not after all preferable to the silo. It was perhaps unfortunate that the harvest saver obtained the gold medal of the Society of Arts, between which body and the Royal Agricultural Society very little love is said to be lost. The harvest saver is applicable also to grain, which the silo is not.

Broadly considered, however, the teachings of the work before us will be very valuable to the farmer.

A Lecture Course in Elementary Chemistry. By H. J. LILLEY, M.A. London: Simpkin, Marshall, and Co.

THIS is another of those small elementary works which have been so numerous during the past twenty years. It contains substantially the same matter and suggests the same questions. The author does not, as far as we perceive, indicate any especial *raison d'être* for his work, or point out any feature which is not common to other treatises of the same class.

The following passage may be pronounced misleading: "Sodium and potassium salts impart a lilac and yellow colour respectively to a flame in which they are vaporised." The words "lilac and yellow" require to be placed in an inverted order, since a pupil reading the passage as it stands might carry away the impression that sodium salts give the lilac and potassium salts the yellow colour.

Mention is elsewhere made of Pettenkofer's suggestion of the use of hydrogen peroxide for restoring oil-paintings. Unfortunately this expedient has proved unsafe; sometimes it fails, and in others it destroys the picture altogether.

There is no mention of spectral reactions as a means of chemical diagnosis.

CORRESPONDENCE.

CHARLES BELL (DECEASED).

To the Editor of the Chemical News.

SIR,—Kindly insert the following advertisement in your next issue:—

BELL, CHARLES.—Would any friend or relation of Mr. Charles Bell, of London, Copper Assayer, kindly communicate with Karl Renouf, Linden Villa, 29, St. Saviour's Road, Jersey.

In sending you the above I should like to add some further facts for your information, in case you might kindly see your way, through your columns or otherwise, to give me any hints or suggestions.

The Charles Bell in question has recently died abroad, and left no clue to his relations, and, as his only known correspondent, I have been communicated with.

My knowledge is limited to the fact that I was a fellow traveller with Mr. Bell during last May, when we met at Marseilles, and he then informed me that he had been with a firm of assayers in London, and had just come from Spain, whither he had gone at the request of a Spanish copper mining company to test some copper ore at the mines.

I believe he was then on his own account, and that the mining company paid his expenses. This I do know,

that he found the lode very rich, even richer than he expected, as the company had sent him a sample to London, but the one he himself drew from the mines was still better.

Unfortunately he never told me the name of this mining company, or that of the firm of assayers with whom he had been when in London. I have applied to several well-known assayers for news, but without success, and I therefore send you the advertisement, trusting it will reach the eye of someone who knew Mr. Charles Bell who will communicate with me.—I am, &c.,

KARL RENOUF.

Linden Villa, St. Saviour's Road,
Jersey.

ON THE ORGANISATION OF SCIENCE.

To the Editor of the Chemical News.

SIR,—While thanking you for your sympathetic review of my pamphlet, I must ask your permission for space to point out that one paragraph in your review is calculated to cause some little misapprehension; for you say that "upon one important point" (viz., the "dissociation of the Literary and Philosophical societies of our large provincial cities") "the author does not touch." If you will do me the favour to refer to pp. 21–23, you will see that I have discussed this question, and have strongly advocated that all these provincial Philosophical and Royal societies, which receive papers upon a dozen different subjects, should "*cease to exist as such*" (p. 22), and resolve themselves into local sections of the Physical, Chemical, Linnean, Geological, and other societies. It being suggested that all these London societies should form local sections on the model of the Chemical Industry Society. I admit, however, that I have said nothing as to the *literary* side of these societies, and that presumably led to your reviewer's remarks.

(I hope that I shall not raise a hornet's nest by suggesting—but, anyhow, I must take the risk—that the various provincial Philosophical and "Royal" societies alluded to above *should cease to exist as such*. . . . Let them dissolve; they will have done their work, and done it well; but they must not stand in the way of better organisation of science."—Page 22).

Apologising for trespassing on your space.—I am, &c.,

"A FREE LANCE."

London, Sept. 24, 1892.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I observe in the current number of the CHEMICAL NEWS a paper by Mr. William Johnstone, who styles himself "Emeritus Fellow of the Institute of Chemistry."

I beg to inform you that Mr. William Johnstone is not a Fellow of the Institute, and that no such title as Emeritus Fellow of this Institute exists.

Mr. Johnstone was a Fellow of this Institute, but his name was recently removed from the Register by the Council; such removal was not upon a ground involving any imputation upon his professional capacity or personal character, but upon the view of the Council on the professional conduct of the plaintiff on one occasion.

Mr. Johnstone brought an action against the President and Members of the Council, in which he sought to prevent the removal of his name from the Register and claimed an injunction and damages. The action was settled in Court, the record being withdrawn without costs on either side upon Mr. Johnstone undertaking not to use in future the title of Fellow or Member of the Institute.—I am, &c.,

G. H. ROBERTSON,

Registrar to the Institute of Chemistry.

9, Adelphi Terrace, Strand, W.C.
Sept. 28, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., Nos. 9 and 10.

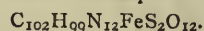
These numbers contain no chemical matter.

Vol. cxv., No. 11, September 12, 1892.

Combustion-Heat of Glycolic Acid.—M. Berthelot. —The conversion of acetic acid into glycolic acid disengages +40.2 cal. in place of +20.6, and the change of acetic acid into glyoxylic acid gives +79.4 cal. or 39.7×2 . This rectification removes an anomaly.

Ptomaine obtained by the Culture of Micrococcus Tetragenus.—Dr. A. B. Griffiths.—This micrococcus is quickly isolated from the sputa of phthisical patients; its elements are spherical cocci of from 1μ to 1.5μ in diameter. It is easily cultivated upon all media. If pure cultures of this microbe are cultivated for several days upon peptonised gelatin a ptomaine is produced. It is a white, crystalline solid, forming prismatic needles. It is soluble in water with a slightly alkaline reaction; it forms a hydrochlorate, a chloraurate, and a chloroplatinate all crystalline. It is also precipitated by the phosphomolybdic, phosphotungstic, and picric acids. Nessler's reagent gives a green precipitate; tannic acid a maroon precipitate, which is slightly soluble. Its composition is $C_5H_6NO_2$. It is poisonous, occasioning death in 36 hours.

On Echinochrome: a Respiratory Pigment.—Dr. A. B. Griffiths.—In 1883 Dr. McMunn discovered a brown pigment in the perivisceral fluid of certain Echinoderms (*Echinus esculentus*, *Strongylocentrotus lividus*, &c.). This pigment, which he named echinochrome, has a respiratory function. It exists in two states: as oxyechinochrome charged with active oxygen, and reduced echinochrome deprived of active oxygen. Dr. Griffiths assigns to echinochrome the empirical formula—



It is partly soluble in water and in alcohol. If boiled with the mineral acids it is transformed into hæmatoporphyrine, hæmochromogene, and sulphuric acid. It possesses certain characters analogous to those of hæmoglobine and chromocruorine.

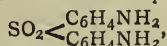
Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., No. 12.

Novel Salts of Iron.—Marcel Lachaud and Ch. Lepierre.—The author's general manner of operating is as follows:—He melts 1 mol. ammonium sulphate and 1 mol. H_2SO_4 up to tranquil fusion (121°). Into the liquid he throws about one-fifth of ferrous sulphate or of ferrous ammonium sulphate, dry, or preferably hydrated, in which latter case the crystals obtained are finer. He heats gently to expel the greater part of the water, and continues the heating more or less according to the case, watching the progress with the microscope. There are formed successively several crystalline salts, chiefly insoluble in cold water, which nevertheless attacks them by degrees. The action of hot water is more rapid. To separate these bodies from the excess of ammonium sulphate he casts them in plates, which are allowed to cool, and coarsely powdered; the powder is boiled with an ascending condenser with an equal weight of alcohol; the mass is disaggregated. The hot alcohol is decanted off, having dissolved the acid salt, which crystallises out in fine laminæ. The alcoholic treatment is repeated if necessary, and the product is centrifuged or filtered rapidly to separate the alcohol.

Action of the Alkaline Nitrites upon the Ethers of the Monobromic Fatty Acids.—G. Lepercq.—M. Steiner has shown that a mixture of ethyl monochloroacetate and of potassium nitrite under the influence of a gentle heat gives off nitrogen, nitric oxide, and carbonic acid, whilst potassium ethyloxalate is formed. The author seeks to show that this salt is not the sole product of the reaction, and that there is likewise formed a nitrogenous body.

On Diamidosulphobenzide and some of its Derivatives.—Ch. Lauth.—Diamidosulphobenzide,—



readily yields diazo-derivatives by the action of nitrite in presence of hydrochloric acid; and these derivatives, if treated with the usual reagents, produce beautiful colouring matters, oranges, scarlets, and browns. Brown and violet tetrazo-colours may also be obtained. The various colouring-matters, notwithstanding their beauty, present no important advantages over the products already known, and they have but slight affinities for cotton.

Volumetric Determination of Uric Acid in Urine.—E. Deroide.—The compound of uric acid and of silver has a constant composition, and if we eliminate the xanthic compounds the Haycraft-Herrmann process will be preferable to all others.

New Preparation of Fatty Bromo-Acids.—P. Geniviesse.—The author has obtained by his method monobromo-acetic acid, the dibromo-compound, the α -monobromo-propionic acid, and the normal α -monobromo-butyric acid.

Certain Properties of the Alkaline Earthy Metals.—L. Maquenne.—The author uses in his experiments the amalgams of the alkaline-earthly metals. He obtains barium nitride, N_2Ba_6 , barium carbide, C_2Ba , strontium nitride, N_2Sr_3 , and calcium nitride, N_2Ca_3 .

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 6.

Examination of Ethereal Oils.—A collection of paragraphs for which we must refer to the original.

Turkey Red Oil.—Arthur Wilson.—From the *Journ. Soc. Chem. Ind.*

Determination of Ferric Oxide and Alumina in Phosphates.—R. Jones (*Zeit. Angew. Chemie*).—This paper will be inserted in full.

Determination of the Pentaglykoses in Plants.—W. E. Stone.—From the *Ber. Deut. Chem. Gesell.*

Identification of Phenacetine.—W. Autenrieth and O. Hinsberg (*Archiv. der Pharm.*).—If phenacetine in fine powder is covered with nitric acid at 10 or 12 per cent and heated to ebullition for a short time, the liquid takes a yellow or orange colour, and the substance previously colourless is converted into an intensely yellow nitro-compound.

Reactions of Piperazine.—H. Eckenroth (*Pharm. Zeit.*).—With Nessler's reagent it gives a white, with copper sulphate a blue, with cadmium chloride a white, precipitate, with silver nitrate nothing.

Determination of the Alkalinity of Blood.—Before and during coagulation the alkalinity is less perceptible. The addition of sodium sulphate to prevent coagulation does not affect the reaction.

Quantitative Determination of Cholesteroline.—K. Obermüller.—A method for the separation of cholesteroline from fat.

Detection of Sugar and Carbohydrates in Urine.—M. Jastrowitz (*Deutsch. Medicin. Wochenschrift*).—The urine of the dog, the horse, and the rabbit, are found to contain carbohydrates, and are in a slight degree laevorotatory.

Diagnosis of the Xanthine Substances of Urine.—G. Salomon (*Archiv. Path. Anatomie*).—With an excess of soda-lye, hypoxanthine, xanthine, and guanine, form readily soluble compounds, whilst para- and heteroxanthine yield compounds readily soluble in an excess of the precipitant.

Detection and Determination of Albumen in Urine.—J. A. McWilliam.—From the *British Medical Journal*.

Detection of Arsenic.—C. H. Wolff (*Pharm. Central Halle*).—The author has developed the electric method of Klobulow. The hydride is decomposed by means of the induction spark.

Delicacy of Various Reactions for Arsenic.—C. O. Curtmann.—The Gutzeit reaction in 1 c.c. of a liquid containing 0.0001 m.grm. As_2O_3 gave in an hour no yellow spot. If the quantity of arsenic was 0.001 m.grm. a yellowish spot appeared after the lapse of twenty-five minutes. Hume's reaction gave with silver nitrate and ammonia a precipitate only after six minutes. The gas given off by Fleitmann's process acted upon silver nitrate paper only after thirty minutes.

Determination of the Atomic Weight of Osmium.—K. Seubert (*Liebig's Annalen*).—The author's mean result was $\text{Os} = 190.33$.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vii., No. 77.

On Malting and on Brewing Beers for Keeping.—Ernst Saalfeld.—From the *Transactions of the Institute of Brewing*.

MISCELLANEOUS.

The Institute of Chemistry.—An Extraordinary General Meeting of the Institute of Chemistry of Great Britain and Ireland will be held at 9, Adelphi Terrace, Strand, on Friday, the 7th day of October, at 5 p.m., to receive, and if desirable approve, of the following Report of the Finance and Office Committees which has been adopted by the Council:—

"*Report of the Finance and Office Committees.*—In view of the necessity for providing, in addition to office accommodation, premises upon which the Examination of the Institute can be efficiently conducted, the Finance and Office Committees jointly recommend that the Office Committee be empowered to take steps to secure such premises; and, if necessary, to expend upon the purchase of a lease a sum not exceeding one-fourth of the invested capital of the Institute, and that the President be authorised to sign the necessary documents."

The Spontaneous Oxidation of Humic Acid and Vegetable Mould.—M. Berthelot and G. André.—The progressive elimination of the humic matters of the soil explains the necessity of its incessant renewal by the decomposition of plants and the addition of dung. The total arable soil behaves like a living being submitted to perpetual destruction and renewal.—*Bull. Soc. Chim. de Paris*, Series 3, No. 13.

Microbia at Sea.—According to an eminent medical contemporary, though the atmosphere in mid-ocean is free from microbia this is not the case on board ship. In the state-rooms and in the first and second cabins of the steamer—evidently a "liner" plying between Europe and America—many bacteria were found on short exposures, especially in the saloons after dining hours. In the steerage, where there were 1100 emigrants packed together in filth, many thousand bacilli and micrococci came to luxuriant development on agar plates and in large gelatin tubes.

Scandinavian Congress of Naturalists.—According to the *Chemiker Zeitung* this meeting was this year held at Copenhagen under the presidency of Prof. Julius Thomsen. The Chemical Section elected as its president Prof. P. T. Clève, and as its vice-presidents Prof. O. Pettersson and Prof. S. M. Jørgensen. The principal papers read before the section were "Some Double Haloid Salts of Gold," by Dr. E. Petersen. The compounds Au_2Cl_4 and Au_2Br_4 obtained by Thomsen, but declared non-existent by Krüss and Schmidt, exist in reality. Julius Petersen reported on the physical conditions of the metal-ammonium compounds. Prof. P. T. Clève delivered a discourse on substitutions in the naphthalene series, and gave a historical survey of Kekulé's benzol-formula. Dr. K. Ström discussed the behaviour of isopropylalcohol with sodium ethylate. Prof. S. M. Jørgensen communicated results on certain cobalt-tetramine salts. Prof. H. Kjeldahl reported on the optical rotatory power of certain vegetable albumenoids. H. Schjerwing, the manager of the Ny Carlsberg Brewery Laboratory, communicated researches on certain derivatives of phenylhydrazine. W. Cronquist reported on the examination of explosives, and on the melting-point of paraffin. Prof. O. Pettersson discussed the proportion of carbonic acid in the air, and a method of determining the alcohol in fermented liquids. Herr Larson gave a full account of recent improvements in the production of copper. Dr. A. Langlet described his investigations on some azthine derivatives. Dr. O. T. Christensen doubted the existence of manganese alum. Herr Franke is of the same opinion. Candidate Schleisser reported on the preparation of diazoamido-benzol and on hardening gypsum. Dr. Emil Petersen treated of the electrolytic dissociation-heat of some feeble acids.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1715.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

Introductory.

THROUGHOUT the whole science of chemistry there is possibly no reagent so frequently represented as taking part in various transformations, but of which so little definite is known, as nitrous acid. In many text-books its properties are cursorily discussed in a few lines, while some writers have gone so far as to deny its existence altogether even in the presence of nitric acid. Among the commoner examples of reactions considered to be effected by nitrous acid, it is necessary only to mention the conversion of the primary paraffinoid amines into the corresponding alcohols, the formation of nitroso- and diazo-derivatives, and the preparation of the fulminates. In a previous paper (*Phil. Trans.*, 1891, A, pp. 312-313), it was my endeavour to prove that the solution of certain metals in nitric acid was conditioned by the presence of nitrous acid, and the cause of the chemical change explained on the supposition that the acid is alternately formed and decomposed.

As a fitting corollary to these investigations, it seemed worthy of interest to examine to some extent the validity of this hypothesis by endeavouring to imitate the reactions supposed to take place on solution of the metal, either when no metal is present, or when the metallic salt is either present or absent.

The stability of nitrous acid in presence of nitric acid forms also a part of this research, and, conversely, the stability of nitric acid in absence of nitrous acid is discussed.

In the present, as in my former, investigations, it will be understood that the term nitrous acid is applied to that kind of matter which decolourises potassium permanganate, liberates iodine from potassium iodide, and gives various colour reactions with certain organic bases.

The Formation of Nitrous Acid in Nitric Acid Solution.

Nitrous acid is generally produced directly by the decomposition or reduction of nitric acid effected (1) by heating the acid, (2) by passing nitric oxide or nitrous fumes into it, (3) by electrolysis, or more indirectly (4) by addition of nitrogen peroxide to water; and (5) by decomposition of metallic nitrites with acids. The nature of these several changes, their conditions, and the compositions of the solutions obtained form the main subjects of this investigation.

The Methods of Analysis.

The following process was adopted for estimating the respective amounts of nitrous and nitric acids in presence of one another; the total acidity was determined in the usual manner by means of standard alkali, the nitrous acid by means of potassium permanganate; from the factors thus obtained the amount of acidity due to the nitric acid by itself could be readily calculated. It was found by experience not only in the present but also in previous investigations, that nitrous acid could not conveniently be estimated by the addition of the permanganate solution until it is no longer decolourised, for the oxidation of the nitrous acid at the end of the operation is gradual and not instantaneous. This point does not seem to have been noticed by the writers on quantitative

analysis. Accordingly the method was modified as follows:—The solution of the nitrous acid was added to such a quantity of the standard permanganate, acidified with sulphuric acid, which was judged to be in slight excess over that required to complete the oxidation, and the whole mixture allowed to stand in stoppered bottles for half an hour. The pink liquid was then poured into potassium iodide solution, and the amount of iodine liberated by the excess of the permanganate determined, as customary, by standard sodium thiosulphate solution. There was apparently no risk of any of the nitrous acid escaping oxidation, and thus liberating iodine from the potassium iodide, if the method was carried out as described.

In order to test the accuracy of the process, some purified silver nitrite was re-crystallised several times from water, a known quantity of it was weighed out, suspended in water, and decomposed by a slight excess of purified sodium chloride. The amount of nitrous acid calculated as (NO₂) was determined in the solution, and for a test analysis the following may be cited:—

Amount of (NO ₂) in 1 c.c. calculated from the weighed quantity of silver nitrite taken	0.005963 grm.
Amount of (NO ₂) in 1 c.c. found ..	0.005974 "

The process is therefore accurate in this particular case to within 1 part in 600. When smaller quantities of nitrous acid were to be estimated, the metaphenylene-diamine method was adopted, the colouration produced being compared with a solution containing a known quantity of nitrous acid by means of the form of tintometer described in my former paper (*vide supra*).

The Stability of Nitric Acid.

It seemed worthy of investigation to determine the actual temperature at which traces of nitrogen peroxide begin to be formed in purified nitric acid of different degrees of concentration; hitherto only general statements are given in the text-books.* Samples of acid of specific gravity 1.5 and 1.4 respectively were purified by the method of blowing a current of air at a temperature of 35°, and thus obtained quite colourless; the latter was diluted (1) with its own volume, and (2) with three times its volume, of water. An acid of specific gravity 1.53 was prepared by distillation of re-crystallised nitre with sulphuric acid, and the reddish-yellow acid thus obtained was re-distilled with an equal bulk of sulphuric acid. A number of attempts were made to render this acid colourless by a current of air or carbonic acid, but, notwithstanding several modifications, these proved unsuccessful. Recourse was, therefore, had to distillation *in vacuo* in an apparatus specially constructed of glass.

The method of operation was as follows:—The slightly yellow acid was placed in a distillation flask, and the receiver kept cooled by a freezing mixture; at a temperature of 45°, and under a pressure of 15 mm., the acid passed over without any visible ebullition: After one-third of the liquid had been condensed, the receiver was changed, and the remainder distilled over; the first portions contained a greater part of the nitrogen peroxide. The second distillate was then re-distilled in the same manner, and thus a perfectly colourless liquid was obtained (specific gravity 0.0=1.541)† containing only

* Carius (*Ber. Dent. Chem. Gesell.*, 1870, p. 690) states that when pure nitric acid of specific gravity 1.51 is heated in sealed tubes at a temperature of 150° and upwards, a reddish-yellow liquid is produced, with evolution of oxygen and "nitrous acid gas;" above 250° the liquid contains such an abundance of nitrous acid that it gives a blue colour on addition of a small quantity of water, and on further dilution nitric oxide is evolved. Accordingly, the decomposition of the acid under these conditions is expressible by the equation $2\text{HNO}_3 = \text{N}_2\text{O}_5 + \text{O}_2 + \text{H}_2\text{O}$.

† I am indebted to my colleague Dr. J. Warts for loan of apparatus and assistance in this method of procedure, which both in his and my hands has proved more successful than the air (or carbonic acid), current method, usually described in the text-books, when acids of specific gravity greater than 1.5 are required perfectly

* A Paper read before the Royal Society, June 2, 1892.

0.011 m.grm. of nitrogen peroxide. Attempts to prepare an acid of greater concentration and more free from the peroxide proved unsuccessful.

In the following table are given the amount of nitric acid in 1 c.c. of each of the several samples:

Sample.	Amount of nitric acid in 1 c.c.	Spec. gravity 10/10.
I.	1.350 grms.	1.541
II.	1.1890 "	1.812
III.	1.0763 "	1.420
IV.	0.5183 "	not determined
V.	0.2563 "	"

For each experiment 10 c.c. of the acid were placed in a small piece of combustion tubing, which had previously been cleansed by being filled with concentrated nitric acid and allowed to stand for several hours, generally, over night. The tubes were then rinsed several times with water, and finally with water re-distilled from potassium permanganate. It was hoped that by this method all reducing substances might be completely destroyed. After introduction of the acid the tubes were quickly sealed up and then heated to various temperatures in water or paraffin baths. The experiments were conducted in dull and generally foggy weather, advantageous at least for them, as concentrated nitric acid is decomposed by direct sunlight. At the end of each experiment the 10 c.c. of acid were poured into 100 c.c. of water, and the amount of nitrous acid determined by the metaphenylenediamine method, as explained above; this is then reckoned in terms of nitrogen peroxide, the substance which imparts the yellow tint to the impure acid.

Sample of acid.	Temperature.	Time.	Nitrogen peroxide produced expressed as 0.001 m.grm. in 1 c.c.
I.	30°	90'	0.25
III.	"	"	2.9
IV.	"	"	0.51
V.	"	"	nil

These results show that whereas the amount of nitrogen peroxide present in the most concentrated acid is doubled by heating under the conditions described above, yet the amounts of this same impurity produced in the less concentrated acids are quite inappreciable. A series of other determinations were made at high temperatures, the results of which are given below.

Sample of acid.	Temperature.	Time.	Nitrogen peroxide present. 0.001 m.grm. in 1 c.c.
I.	58°	90'	0.27
III.	"	"	2.7
IV.	"	"	2.9
V.	"	"	not measurable

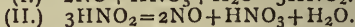
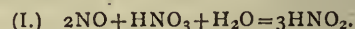
Sample of acid.	Temperature.	Time.	Nitrogen peroxide present.
I.	100°	90'	0.431
III.	"	"	0.05
IV.	"	"	nil
V.	"	"	nil
II.	120°	90'	0.96
III.	"	"	0.2
IV.	"	"	0.2
V.	"	"	nil
III.	155°	90'	0.70
IV.	"	"	0.06
V.	"	"	0.06
III.	195°	5'	2.19
IV.	"	"	80

colourless. The distillation method, however, presents one of two alternate difficulties; on the one hand, in each repetition of the distillation the proportion of nitrogen peroxide is decreased; on the other, that of the water is increased.

It is manifest from the figures given in the tables above that sample No. I was decomposed to some extent at 58°, and to a greater degree at 100°, sample No. II. at 120°, sample No. III. at 155°, and very rapidly at 195°, sample No. IV. at 195°, while the most dilute acid remained practically unaltered throughout. It would also appear that, provided every care be taken to eliminate reducing substances, especially of an organic character, and provided also that the acids are not unduly exposed to sunlight, nitric acid is more stable than former experience indicated. It would be an interesting subject of inquiry to ascertain as to whether nitric acid is affected by shocks, as I have found that samples of acid purified so as to be practically free from nitrous acid were contaminated with that impurity after a railway journey.

Formation of Nitrous Acid from Nitric Oxide and Nitric Acid.

It is a common matter of observation that when nitric oxide gas is passed into nitric acid a greenish-blue solution is produced, which shows all the reactions of nitrous acid; some writers, however, consider that the nitric oxide gas is only dissolved as such in the nitric acid in that, when the liquid is warmed, the gas is again evolved. It is more probable that nitrous acid is formed and subsequently decomposed, changes represented by the following equations:—



Clemente Montemartini (*Rome, Accad. Lincei Rendiconto*, 1890, p. 264), has proved that in these changes the latter proceed quantitatively, at least in dilute solution, in accordance with the equation given.

If these changes are strictly reversible, it would follow as a necessary consequence that there would be a limit to the amount of the nitrous acid produced, and this limit would be dependent upon conditions such as concentration of acid and temperature. The equation for equilibrium will be—

$$p/q = \text{constant},$$

wherein p is the mass of nitric acid, and q is the mass of nitrous acid, for when the limit is reached the amounts of nitric oxide gas passing in and out would be identical, while the alteration of the mass of water would be immaterial.

On the other hand, if the phenomenon is merely that of solution, the amount of nitric oxide gas dissolved should, other conditions remaining the same, diminish under all circumstances as the temperature increases.

To decide between these views, and to determine the limit, whether of nitrous acid formed or of nitric oxide dissolved, as the case might be, a series of experiments were conducted in the following manner.

Nitric acid was passed through an apparatus consisting of (1) a wash-bottle containing soda; (2) a set of Liebig's bulbs; and (3) a set of Geissler's bulbs both filled with nitric acid of the same concentration, the latter of which was used for the analytical determinations; and (4) a wash-bottle containing soda to prevent any nitrous fumes produced by the passage of the unaltered nitric oxide into the air, from accidentally coming in contact with the acid experimented upon. In these and succeeding experiments the apparatus consisted wholly of glass, except for small pieces of rubber tubing which served for connections; these were frequently renewed. Before the nitric oxide was passed, the whole apparatus was filled with hydrogen, my previous experiments having shown that this gas, when ready-made, does not reduce nitric acid, but even mechanically blows off any slight impurity of nitrous acid. At the end of the operation the Geissler's bulbs were quickly detached, and the acid blown out by a rapid stream of carbonic acid. While the experiment was proceeding the bulbs were kept in a water-bath, the temperature of which was carefully regu-

lated; the passage of the nitric oxide was kept as uniform as possible.

The following table contains the results of the first set of experiments; not only of the actual amounts of nitric acid, and of nitrous acid, *i.e.*, the reducing power, are given, but also of the percentage amounts of these acids, taking the total acidity as 100:—

SERIES I.—Temperature, 22.5°.

	Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	4	0.2404	0.0168	93.47:6.53
" "	8	0.2409	0.0164	93.62:6.38

These results show that the phenomenon, whether of reaction or of solution, was complete at the end of the first interval of time; but, taken by themselves, they would not suffice to distinguish under which category the change is to be classified. Accordingly a series of experiments were conducted in which the only variable condition was that of temperature, for, as pointed out above, if the nitric oxide is merely dissolved, then the reducing power would diminish with increase of temperature, but if a chemical change takes place, then its amount would depend upon the relative intensities of the chemical change represented by the equations given:

SERIES II.—Temperature, 9°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	3	0.2496	0.0169	93.66:6.34

SERIES III.—Temperature, 27.5°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	4	0.2336	0.0171	93.18:6.82
" "	8	0.2362	0.0169	93.69:6.31

SERIES IV.—Temperature, 32°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	100:0
After passage of nitric oxide ..	3	0.2318	0.0223	91.22:8.76

SERIES V.—Temperature, 42°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	—
After passage of nitric oxide ..	3	0.2372	0.016	93.68:6.32

SERIES VI.—Temperature, 52°.

	Time. Hours.	Nitrous acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage rates.
—	—	0.2549	nil	—
After passage of nitric oxide ..	3	0.2366	0.0136	94.56:5.44

It will be evident from the above experiments that the ratio of nitrous to nitric acid increases slightly with rise of temperature up to 32°, but from this point it decreases so that the values at 9° and 42° are nearly identical.

(To be continued).

ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANIDES.

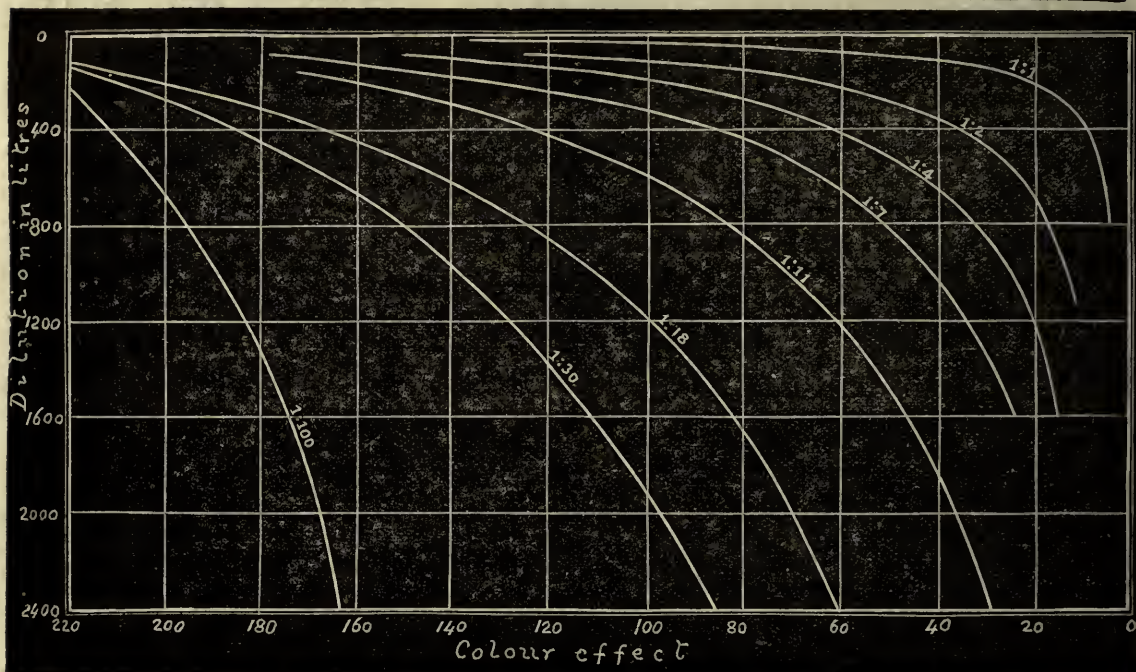
By H. M. VERNON, B.A.

THE colour reactions of various salts with one another were studied at considerable length by Gladstone (*Phil. Trans.*, 1855, 179), with a view to determining whether the quantity of a salt formed in a solution was dependent on the masses of the reacting salts in accordance with the law of mass action, the importance of which was then only beginning to be thoroughly recognised. The reactions of ferric salts with sulphocyanates were chiefly studied, the amount of ferric sulphocyanate formed being determined colorimetrically. The results obtained did not appear to obey the law of mass. As the correctness of the law of mass action has been thoroughly demonstrated by many chemists by numerous series of experiments, made under all possible variations of conditions, it would seem superfluous to bring forward any further proofs of its veracity. It is important, however, that all apparent exceptions to the law should be examined, and if possible adequate explanations for the variations be found, so that the law may be proved universally true, as it should be by theory. The object of this paper is, therefore, to examine the reactions of ferric salts and sulphocyanates under different conditions, so as to determine, if possible, the cause of the variations observed by Gladstone.

The colour comparisons were made in the same manner, and with the same apparatus, as those described by the writer in a paper on "The Dissociation of Electrolytes in Solution" (*CHEMICAL NEWS*, 1892, p. 105). All ferric sulphocyanate solutions were compared with a 0.1 per cent solution of the stain picrocarmine, which consists of a mixture of carmine and picric acid. This solution was of exactly the same tint as those of ferric sulphocyanate, and its use has several advantages over that of a standard solution containing ferric sulphocyanate. In the first place, it suffers no variation in colour with change of temperature, whilst ferric sulphocyanate solutions change considerably. It is not necessary, therefore, to bring this solution to a constant temperature when colour comparisons are made. Again, a ferric sulphocyanate solution does not remain a constant colour on keeping, but becomes lighter, owing to the decomposition of some of the ferric sulphocyanate and the deposition of small quantities of ferric oxide.

The method of determining the amount of ferric sulphocyanate formed differed essentially from that made use of by Gladstone, and indeed it is almost solely to his method that the variations observed by him are due. In the present experiments the solutions were compared by viewing them vertically in flat-bottomed tubes, and varying the thickness of the column of standard picrocarmine solution till of the same tint. In Gladstone's experiments the solutions were viewed horizontally through the sides of two test-glasses, one of which contained a standard solution and the other the solution to be compared. This solution was then diluted with water till of the same tint as the standard solution, and the amount of water so added taken as a measure of the increased amount of ferric sulphocyanate present in the solution. He assumed that the water added had no decomposing effect on the ferric sulphocyanate, and that, for instance, if of two solutions containing equal quantities of ferric sulphocyanate one was diluted to ten times its volume, it would still contain the same quantity of ferric sulphocyanate in solution, and that its tint, when viewed horizontally in a test-glass, would be exactly a tenth of its original value. This supposition was incorrect, as ferric sulphocyanate is very greatly affected by dilution. In the paper before referred to the writer showed that none of the salts examined, on dilution from 1 to 10 litres, decreased in colour more than about 30 per cent. Solutions of ferric sulphocyanate, in some cases,

Trichosantheine.—A. Tschirch (*Schweizer. Wochen-schrift Chem. Pharm. und Chemiker Zeitung*).—Trichosantheine is a green colouring-matter which the author has obtained from a Javanese fruit (*Trichosanthes pubera*). It is interesting as being the first green colouring-matter from the vegetable kingdom which differs decidedly from chlorophyll. The "thallochlo" which Berzelius obtained from the gonidia of *Cetraria islandica*, and which he regarded as a distinct vegetable colouring-matter, has been proved by Tschirch to be identical with chlorophyll.



show a colour decrease of nearly 90 per cent when rendered ten times more dilute.

The effects of dilution on solutions of ferric sulphocyanate were first of all examined fully with solutions containing, to 1 part of potassium sulphocyanate, 1, 2, 4, 7, 11, 18, 30, and 100 equivalents respectively, of ferric chloride. The colour value of a solution containing 1 c.c. of decinormal potassium sulphocyanate solution and 1 c.c. of equivalent decinormal ferric chloride solution diluted to 8 c.c., that is at a dilution of 80 litres, was taken as 50, and the other values were calculated against this. Measurements could not be made for more concentrated solutions than those of 40 litres dilution, as the tint of the solution was too dark. In most cases even 1 c.c. of decinormal KSCN to 100, 30, &c., equivalents of ferric chloride produced too deep a colour, so half this quantity had to be worked with. Solutions of several different strengths of all the salts used were prepared, so that the accuracy of the composition of the ferric sulphocyanate solutions might not be impaired by having to take too small volumes of the component solutions for correct measurement. All the solutions used were made up of equivalent strength, so that a normal solution of ferric chloride would only contain a sixth of its molecular weight, Fe_2Cl_6 , in grms., diluted to 1000 c.c. All the comparisons were made at 20°C . Most of the solutions were compared at about twenty different dilutions varying from 40 to 2400 litres. It was not possible to examine solutions containing only one or two equivalents of ferric chloride at a greater dilution than 800 litres, as the tint of the solution became too light, and also the colour alters somewhat from red to reddish yellow.

In the figure are given, diagrammatically, the colour values obtained for the different solutions. It will be seen that the more ferric chloride there is present in a solution, the more stable is the ferric sulphocyanate with regard to dilution. Even in the solution containing 100 equivalents the decrease of colour is considerable. Thus on dilution from 160 to 2400 litres the colour decreases from 222.8 to 162.6, or 27 per cent. With the 1:30 solution the colour decrease, for the same dilution, is over 60 per cent, and with the 1:18 solution about 73 per cent. In fact, it will be seen from the figure that the stability of

ferric sulphocyanate on dilution varies regularly with the amount of ferric chloride the solution contains. The 1:1 solution is therefore the most unstable of all, the colour decreasing about 94 per cent on dilution from 40 to 640 litres.

As was expected, the amount of ferric sulphocyanate formed in those solutions was found to vary with the amount of water present in accordance with the law of mass.

In the table are given the ratios for the value of the different solutions calculated on the formula—

$$\frac{1}{\theta} \times \frac{a}{A-a},$$

where θ is the concentration of the solution, A the colour value at infinite concentration, and a the colour value at the concentration θ . In accordance with the law of mass all the ratios calculated for each solution should be equal. At dilution A are given the numbers which were found by trial to agree best with the experimental values. These values must be taken as representing the true amounts of ferric sulphocyanate formed in the presence of varying quantities of ferric chloride, when no water is present to cause dissociation. They show that if no water were present, or if no dissociation took place, a solution containing ferric chloride and potassium sulphocyanate in equivalent proportions would contain twice as much ferric sulphocyanate as a solution containing 100 equivalents of ferric chloride. The action of ferric chloride on a solution containing ferric sulphocyanate is thus twofold. On the one hand, it exerts a decomposing action, it perhaps tending to form a basic salt, of less colour effect; whilst, on the other hand, it forms a solution which does not cause the dissociation of the ferric sulphocyanate to the same extent as pure water does; so in most cases, on its addition, the amount of ferric sulphocyanate formed increases. A very concentrated solution of ferric sulphocyanate would show a decrease in colour on the further addition of ferric chloride, and not an increase. If the curves in the figure are produced, it will be seen that at a dilution of 100 litres the colour values of the 30 and 18 equivalent solutions would be greater than that of the 100 equivalent solution.

Dilution in litres.	Proportion of Ferric Chloride to 1 part Potassium Sulphocyanate								
	100	30	18	11	7	4	2	1	
A	230	240	250	255	303	365	400	450	
40	—	—	—	—	—	—	—	—	0.118
80	—	—	—	—	—	—	—	—	0.125
120	—	—	—	—	1.85	0.853	0.456	0.125	
160	59.2	17.1	10.02	4.14	1.98	0.876	0.474	0.119	
200	57.5	16.6	10.07	4.24	2.00	0.871	0.467	0.118	
240	60.5	16.0	9.63	4.38	1.98	0.923	0.427	0.116	
280	56.5	16.7	9.18	4.62	2.01	0.997	0.494	0.115	
320	57.5	15.8	9.08	4.56	2.00	0.995	0.479	0.101	
360	59.2	16.3	9.00	4.50	1.97	0.993	0.496	0.102	
400	58.8	16.7	9.26	4.51	1.93	0.991	0.473	0.101	
480	61.3	16.3	10.06	4.69	1.93	0.986	0.441	0.096	
560	60.5	15.6	10.03	4.83	1.98	0.978	0.448	0.092	
640	60.0	14.7	9.04	4.77	2.04	0.955	0.493	0.092	
720	52.5	14.9	9.60	4.48	2.01	0.939	0.435	—	
800	57.1	14.7	9.27	4.82	2.01	0.910	0.402	—	
960	54.0	16.4	10.10	4.73	2.02	0.902	0.401	—	
1120	56.5	17.3	9.67	4.55	1.92	0.929	—	—	
1280	60.7	17.1	9.89	4.63	1.81	0.936	—	—	
1440	68.4	16.9	9.00	4.53	1.91	0.958	—	—	
1600	54.9	16.7	9.79	4.39	1.90	0.954	—	—	
1760	58.4	16.8	9.05	4.40	—	—	—	—	
2080	67.0	16.4	10.11	4.11	—	—	—	—	
2400	68.9	16.4	9.34	4.41	—	—	—	—	

It is evident, therefore, that the law of mass plays a different part in the formation of ferric sulphocyanate from that accorded it by Gladstone, the increase of colour on the addition of excess of ferric chloride being merely due to the fact that the dissociation of the coloured salt is decreased to an extent great enough to overpower the effect due to the actual decomposition of the salt.

From the table it will be seen that the values for the decrease of colour effect on dilution obey the law of mass fairly regularly. The ratios for the 1:100 solution show greater variations than those for the other solutions, as the number calculated for A is but slightly larger than the experimental numbers obtained at other dilutions, and so a small error becomes considerably magnified. Thus an increase of 1 per cent in the colour value found at dilution 10 would cause the ratio in the table to increase from 59 to 67. The extreme ratios do not, in fact, indicate an error of more than about 2 per cent in any of the colorimetric measurements. This is as accurate as one can hope to make such determinations, and it is only after considerable practice that the eye can judge to within these limits. The solutions containing 30 and 18 equivalents of ferric chloride gave moderately regular values; but solutions containing 11, 7, 4, and 2 equivalents respectively, give values which are rather less for the small and great dilutions than for the moderate dilutions. This may perhaps be due to experimental error for the 11, 7, and 4 equivalent solutions, but it seems too large and well-marked to be put down to this cause in the case of the two equivalent solutions. What it can be due to is not known; but it must be remembered that the solutions do not contain merely ferric sulphocyanate in a more or less dissociated state, but also potassium chloride and undecomposed ferric chloride, and it is possible that the variations may be due to some secondary actions taking place between these salts. The solution containing equivalent quantities of ferric chloride and potassium sulphocyanate gives values which show a slight decrease as dilution proceeds. Whatever value for A the colour numbers are calculated against, it is found that the ratio values always showed a decrease for the more dilute solutions, the value 450 giving the least decrease. This value 450 must be taken as the colour the ferric sulphocyanate would show in a solution if it were unaffected by the presence of water or other salts, for in the equal equivalents solution at infinite concentration there can only be present potassium chloride besides the ferric

sulphocyanate, and it is not probable that this salt would have any decomposing effect. As therefore, at a dilution of 640 litres, the colour value is only 5.1, the solution only contains about a ninetieth part of the possible quantity of ferric sulphocyanate. That ferric chloride and potassium sulphocyanate, in equivalent quantities, react almost completely at infinite concentration to form ferric sulphocyanate, is proved by comparing their colour effect with that of a solution containing only ferric sulphocyanate. Such a solution was prepared by mixing equivalent quantities of barium sulphocyanate and ferric sulphate solutions, and allowing the precipitated barium sulphate to subside. This solution possessed a colour effect almost the same as that of a solution of equivalent quantities of ferric chloride and potassium sulphocyanate, and also it was affected to the same extent by dilution. Thus at a dilution of 40 litres the colour effect was 84.3; at 80 litres, 50.7; at 160 litres, 24.2; and at 400 litres, 8.7. The colour values of the ferric chloride and potassium sulphocyanate solution, at the same dilutions, are 86.0, 50.0, 25.3, and 8.9 respectively.

A similar series of determinations to the above was then made, in which the proportion of ferric chloride was kept constant, and that of the potassium sulphocyanate varied. It was thought that the values obtained would probably be of the same order as the previous series, but such did not prove to be the case. Solutions containing to one equivalent of ferric chloride 100, 30, 18, 11, 7, 4, 2, and 1 equivalents respectively of potassium sulphocyanate were examined at the same dilutions as the former series. As the numbers obtained do not serve as an illustration of the validity of the law of mass, in that they decrease at a greater rate than in proportion to the quantity of water added, they are not given here. The cause of this greater decrease was not discovered. It may have been due to a trace of impurity in the sodium sulphocyanate. So unstable is the coloured salt that the substitution of tap water for distilled water in a solution may decrease the colour effect by more than half.

(To be continued.)

THE SYNTHESIS OF SUGARS.*

By W. E. STONE, Purdue University.

(Continued from p. 166).

FISCHER'S next step was to renew his studies upon one of the natural sugar bodies, *viz.*, mannitol. This, as was already known, was converted by oxidation, first into the aldehyd, mannose, and then into the monobasic mannonic acid, $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH}$. This acid, however, had not been well studied, owing to the difficulty of isolating it. Here again the versatile reagent, phenylhydrazin, came into play, producing with the acid, in mixture with impurities, a crystallisable "hydrazide" from which the pure acid was afterwards obtained as a lactone (*Berichte der Deutschen Chemischen Gesellschaft*, xxii., 2728, 3219).

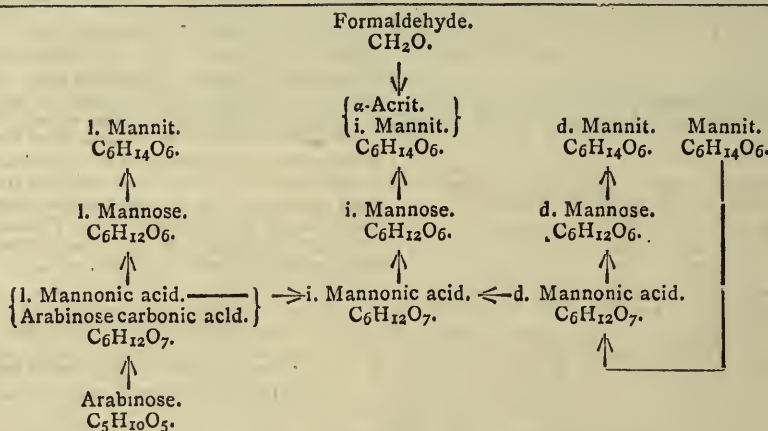
A wide gap in our understanding of the relations between different sugars was bridged when it was recognised that this mannonic acid lactone was isomeric with the arabinose-carbonic acid lactone already referred to. Here again appeared a remarkable difference in the optical properties of these isomers, which were otherwise practically identical. The mannose derivative was *dextro-rotatory*, and the arabinose derivative *levo-rotatory*. Moreover, when these optically opposed isomers were brought together in watery solution, in molecular proportions, they united to form a new lactone, like the others in all respects, save that it was *optically inactive* (*Berichte D. Ch. G.*, xxii., 370). This corresponds entirely with the well-known relation between the active and inactive modifications of tartaric acid.

* *Agricultural Science*, vi., No. 4.

Fischer now had in hand three related isomeric acids of the sugar group. His next step was to reduce them by sodium amalgam in acid solution to their corresponding aldehyds (*Berichte D. Ch. G.*, xxii., 2204, and xxiii., 930). In this way were obtained three isomeric aldehyd sugars, corresponding to the acids from which they were derived—one dextro-rotatory, one lævo-rotatory, and one inactive. These aldehyd sugars were further reduced to their corresponding hexatomic alcohols, retaining in each case their characteristic optical properties.

The significance of this optical series of isomers now became very great, since it strongly argued the possibility that all the natural sugars, previously known in only one form, might actually exist in optically opposed, or even inactive, isomeric forms, thus greatly increasing their possible number.

The completion of this series by the production of the inactive mannit led to the astonishing fact that it was identical with the α -acrit obtained synthetically from formaldehyd; and that here the synthetical and natural derivatives met. To distinguish between these dextro, lævo, and inactive isomers, Fischer adopted the prefixes d., l., and i., respectively. The following diagram will make the relation between these derivatives apparent (*Berichte D. Ch. G.*, xxiii., 2131.—Adapted).

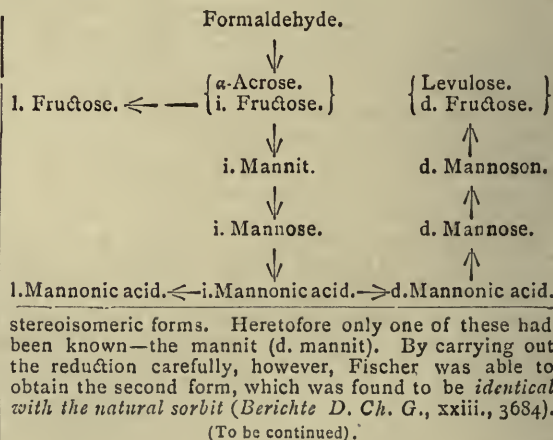


Mention has already been made of the separation of the α -acrose from its impurities as the α -acrosazon from which the sugar was regenerated. This α -acrose was optically inactive, but otherwise identical with levulose, or, as Fischer designates it, *fructose*. The synthetic α -acrose was, therefore, i. fructose (*Berichte D. Ch. G.*, xxiii., 384, 387). This completed, therefore, the synthesis of a regular member of one of the groups of sugars, although the product was not a body previously known. It remained now to show how the transition from the inactive synthetic product to one of the optically active natural sugars could be made. The i. mannonic acid had been prepared by combining the d. and l. mannonic acids. It now became Fischer's task to decompose an optically inactive body into its active components, or by destroying one to set free the other. For this purpose he made use of Pasteur's device of subjecting the synthetic i. fructose to fermentation, and found in fact that the yeast destroyed only one of its components, *viz.*, that which rotated to the left, leaving behind the dextro-rotatory member (*Berichte D. Ch. G.*, xxiii., 389). The yeast had acted upon the mixture in such a way as to remove the natural or lævo-fructose, rejecting its optical opposite. The latter, although dextro-rotatory, is classified by Fischer as l. fructose, while the natural fructose, although lævo-rotatory, is called by him d. fructose, for the purpose of bringing all the natural sugars into the "d." series, where indeed they all come naturally with the exception of fructose.

The last operation, while it yielded a new sugar, failed to close the gap between the synthetic and natural sugars, and recourse was again had to a new method (*Berichte D. Ch. G.*, xxiii., 389). Starting where the synthetical processes had ended, with the α -acrit, or i. mannit, this was converted by oxidation into i. mannonic acid. By preparing from this its strychnine salts, it was separated into the d. and l. mannonic acids, and these, by means of sodium amalgam, were reduced to the d. and l. mannose respectively. The d. mannose was converted into the d. mannosazon, and this in turn into the d. mannoson, which on reduction yielded, *not d. mannose, as might have been expected, but d. fructose*, identical with the natural fructose or levulose. This effected the complete synthesis of a natural sugar. The diagram below will illustrate the different steps of the operation.

On referring to the previous diagram, it will be seen that all the intervening stages between formaldehyd and the natural levulose and mannit had been taken, and in addition to this the heretofore entirely unknown and unsuspected inactive and lævo-modifications of these had been discovered.

By reduction of fructose to the corresponding hexatomic alcohol, the characteristic ketone group becomes asymmetrical, and the alcohol should theoretically have two



Borough Road Polytechnic Institute.—A class for the study of the Manufacture of Oils and Colours, and of Oils and Fats, commenced at the above Institute on Tuesday, Oct. 4. The class will be conducted by Mr. J. G. McIntosh, for whom a small laboratory has been specially fitted up to enable students to gain something more than mere book knowledge.

ON A FOSSIL WOOD CONTAINING FLUORINE.

By Dr. T. L. PHIPSON, F.C.S., &c.,

Graduate of the Faculties of Science and Medicine of the University of Brussels.

WITH regard to the notes published recently in the *Comptes Rendus* of the Paris Academy of Sciences by Adolphe Carnot, and more particularly the one entitled "On the Composition of Fossil Bones and the Variation of the Amount of Fluorine contained in them in different Geological Strata," I wish to state that thirty years ago I made the analysis of a fossil wood from the Isle of Wight which yielded 32.45 per cent of phosphoric acid and 3.90 of fluorine. It had the following character:—Colour, brown; structure of wood, ductile; specific gravity = 2.71; locality, in the green sand (cretaceous) of the Isle of Wight. The specimen which found its way into my laboratory weighed over 4 lbs. The complete analysis showed that it had been fossilised by phosphate of lime and fluor-spar; had it been an ordinary mineral substance, it would have been looked upon probably as a mixture of apatite and fluor-spar. In spite of its enormous age, it contained 6.62 of organic matter. This organic matter might certainly have been due to infiltration, but the fossil *teredos* which I took with my own hands from the Brussels tertiary sands gave a distinct odour of the sea when the rock containing them was broken with the hammer.

Laboratory of Analytical Chemistry,
Putney, London, S.W.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

THE author proposes certain procedures in which use is made of hydrogen peroxide.

Concerning the decomposition which takes place on the action of chromic acid or a chromate upon hydrogen peroxide in presence of free acid, there have prevailed in part contradictory views. The exact knowledge of this reaction has obtained a higher significance for analytical chemistry since Carnot brought it into use for the determination of chromic acid. The same reaction has been further recommended for the determination of hydrogen peroxide, though A. H. Allen and G. Lunge have pointed out that the percentage of hydrogen peroxide in a solution cannot be accurately determined with chromic acid, as the reaction with an excess of chromic acid does not take place smoothly and completely.

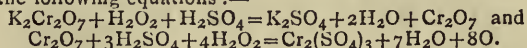
According to H. Aschoff, on the action of hydrogen peroxide upon an acid solution of potassium bichromate, so much oxygen is liberated that 8 atoms of oxygen go to 1 mol. of potassium bichromate.

On the other hand, Berthelot, who has closely studied the behaviour of hydrogen peroxide with chromic acid, finds that such a decomposition occurs only if the solution of chromic acid is allowed to flow slowly into the solution of the hydrogen peroxide. If we proceed inversely and pour the hydrogen peroxide gradually into the chromic acid only 6 atoms of oxygen are set at liberty.

According to the numerous experiments of Baumann and Lübcke the statements of Berthelot do not hold good on working with strongly diluted solutions in presence of an excess of sulphuric acid and mixing the reacting substances at once. On the contrary, Baumann and Lübcke confirm the results of Aschoff.

Hence the reaction between chromic acid and excess of hydrogen peroxide in largely diluted solutions mixed

with an excess of sulphuric acid take place according to the following equations:—



The chromic acid is therefore first converted into per-chromic acid, which is then reduced by the hydrogen peroxide to chromium oxide, whereby half of the oxygen given off is derived from the hydrogen peroxide. After the manner of the decomposition of chromic acid has been placed beyond doubt for all cases which come under consideration in the methods to be described below, it has become possible to determine a greater number of substances by gas-analysis.

In these gas-volumetric determinations Baumann, as regards the apparatus to be employed, lays particular weight upon the point that both the gas burette and the generating vessel are under water. Hence he recommends as previously, in the valuation of manganese by the gas volumetric method, P. Wagner's azotometer. Baumann uses also a modification of Wagner's apparatus, distinguished by its simplicity. The author avoids the use of reduction instruments of any kind, as they complicate the analysis in a quite needless manner and still afford no absolute certainty for the correct calculation of the results. It seems most convenient to work out accurate special tables, and some such have been already calculated by Lübcke.

1. *Determination of Chromic Acid.*—The liquid containing the chromic acid, which must not be too concentrated, and should be in volume from 10 to 50 c.c., with 10 c.c. of dilute sulphuric acid (1:5), is placed in the wide space of the generating vessel. The small glass cylinder melted to it is charged with from 5 to 10 c.c. of commercial hydrogen peroxide. After the generating vessel has stood for ten to fifteen minutes in water of the temperature of the room, and the water stands at an equal height in both limbs of the U-tube of the measuring apparatus and reaches exactly 0 in the measuring tube, the hydrogen peroxide is poured into the solution of chromic acid.

Water is now allowed to flow out of the measuring apparatus, taking care that during the development of the gas the liquid stands rather lower in the tube which is not graduated. It is shaken round well, the cock over the generating vessel being kept closed during shaking and opened only for a short time, always after shaking for about half a minute, until the chief quantity of the oxygen has been liberated. Almost the entire quantity is set free in the first two minutes. In order to expel the rest (about 1 c.c.) powerful shaking is required for about five or six minutes. If no further increase of volume is perceptible in the measuring tube, the generating vessel is returned to the water-trough, and after the lapse of ten to fifteen minutes, and after the level of the water in the tubes of the measuring apparatus has been equalised, the volume of gas is read off.

This volume is reduced to 0°, and 760 m.m. of the barometer by a simple multiplication, according to Baumann's "Tables for Gasometry" (Munich: Reiger). If the number found is multiplied by 2.246 we find the weight of the chromic acid sought for (CrO_3 in m.grms.), as 1 c.c. of oxygen corresponds to 2.246 m.grms. CrO_3 ; or we may use the table of L. Vanino. We have then to multiply the volume of oxygen as read off with the number in the table, and then the product with 1.5716, as 1 m.grm. oxygen corresponds to 1.5716 m.grm. chromic acid. The results obtained by the author in this manner are very satisfactory.

The gas-volumetric determination of oxygen can also be effected with hydrochloric acid instead of sulphuric acid. The quantity of free hydrochloric acid for an experiment must not, however, exceed 4 c.c. of dilute hydrochloric acid (1:2) to 40 c.c. of the dilute solution of chromic acid, as otherwise errors may be occasioned by the liberation of chlorine, and more gases may be evolved than corresponds to the theoretical value.

* *Zeit. für Angew. Chemie und Zeit. für Analytische Chemie.*

The presence of nitric acid does not interfere if its quantity does not exceed 0.2 grm. in the solution examined. Larger quantities diminish the results, since only 7 to 7.5 atoms of oxygen are set free for each mol. of bichromate.

According to Lübecke the injurious influence of nitric and hydrochloric acid is diminished by the presence of free sulphuric acid. Acetic acid and succinic acid do not interfere with the reaction. Such organic substances as are readily oxidised by chromic acid (tartaric acid, oxalic acid, sugar, alcohol), prevent an accurate determination of chromic acid or render it quite impossible.

By means of the gas-volumetric determination of chromic acid it is possible in a convenient manner to find the standard of a solution of potassium bichromate without the aid of a balance or of other standard solutions. Here we have to consider that not all the oxygen evolved is derived from the chromic acid. Of the eight atoms of oxygen liberated from a molecule of bichromate only three are to be ascribed to the oxidation value of the solution of potassium bichromate.

The standard of such a solution is obtained by first multiplying the volume of gas given off with 0.375, and then re-calculating the volume into weight by the aid of Vanino's table.

(To be continued).

DETERMINATIONS OF TANNIN ACCORDING TO GANTLER'S PROCESS.

A. KLINGER and A. Bujard come to the same conclusions as von Schröder and Pässler. The authors on their part confirm the statement that the consumption of permanganate by tanniniferous solutions after the tannin has been precipitated with hide-powder cannot by any means be neglected, as Gantler asserts. If the filtrate from hide is neglected, in case of oak bark, they obtained 5 per cent of tannin in excess. As the hide-powder used generally contains soluble organic substances, its consumption of permanganate must be determined and subtracted.

As regards the objections of Procter, the authors found that certainly, as he alleges, an increased addition of sulphuric acid involves an increased consumption of permanganate, but only up to a certain limit. Klinger and Bujard used, according to Gantler's directions, 10 c.c. of sulphuric acid (1:5). On the addition of 20, 25, and 30 c.c. of sulphuric acid, A. Baier found the proportion of tannin increased by 2 per cent; a further increase of the addition (40 and 50 c.c.) had no perceptible influence on the last result.

In opposition to Procter's observation, that in one and the same extract of bark the consumption of permanganate varies as much as 2.2 c.c., the authors have always obtained results which agreed very well with each other.

The objection of Procter that any gelatinous constituents of the hide-powder had a great influence on titrating according to Gantler, whilst on titrating according to Löwenthal this is not the case, was found by the authors to be verified; but if, as they propose, a blank experiment is first made with hide-powder, this circumstance does not occasion an error.

The authors have by opportunity of these experiments determined the proportion of tannin in a new tannin material. It is the root of canaigre (*Rumex hymenosepalus*), a plant growing in Lower California, and much used in Texas for tannin. In the root, when dried at 100°, the authors found tannin:—

According to Löwenthal	33.62
„ Gantler	42.14
„ the gravimetric method ..	40.80

—Zeit. für Analytische Chemie.

THE ACTION OF BARIUM PEROXIDE UPON METALLIC SALTS.

By W. KWASNIK.

NOT merely potassium ferricyanide, but a large number of other salts, act upon barium peroxide so as to liberate oxygen. The salts of the alkalies and alkaline earths do not liberate oxygen. Salts of magnesium act in this manner very slightly, and those of zinc and cadmium but little. Salts of nickel and cobalt occasion a vigorous development of gas, as do also the salts of iron, manganese, chrome, and aluminium. The hydroxides of the respective metals are formed, and half the oxygen present in the barium peroxide is set free. In the lower salts of the latter group the reaction takes place in two phases. An oxidation firstly takes place, and afterwards gaseous oxygen is liberated.

Cupric salts produce at once a brisk escape of oxygen.

By the salts of mercury, silver, and gold for each molecule of barium peroxide 2 atoms of oxygen are set free and the metallic salts are reduced. Platinum forms an exception from the behaviour of the precious metals just mentioned. If platinum chloride is used there is formed a soluble compound analogous to potassium platinum chloride. The double chlorides of platinum and an alkaline or alkaline earthy metal do not act upon barium peroxide. Platinum chloride (PtCl_4) and argento-platinum chloride ($2\text{AgCl}, \text{PtCl}_4$) are decomposed with separation of platinum or platinum and silver.

Barium peroxide yields oxygen not merely with soluble metallic compounds, but with such as are insoluble, although in the latter case the development is much slower. In many compounds the application of heat is necessary.—Zeit. für Analytische Chemie.

SEPARATION OF IRON FROM THE ELEMENTS BY A NEW PROCESS.

By J. W. ROTHE.

THE process is founded on the fact that all ferric salts, on repeated shaking out with ether in a hydrochloric solution at a proper concentration of the hydrochloric acid, give off all their iron to the ether in the form of ferric chloride.

Ferrous salts, under similar conditions, are not extracted by ether.

Manganous, nickelous salts, as well as the salts of chrome and aluminium, if shaken up in a similar manner do not yield any compounds soluble in ether.

Cobaltous and cupric salts are dissolved in variable quantities by ether, according to the respective proportions of these salts in the hydrochloric solutions; but the quantity of cobalt and copper dissolved is relatively very trifling. If the ethereal iron solution is then shaken up with hydrochloric acid solution of specific gravity 1.104, these slight impurities of cobalt and copper may be removed. Slight proportions of ferric chloride may certainly pass again into the hydrochloric solution and must be removed by again shaking out with ether.

In the application of this method to the examination of steel and iron certain conditions have to be observed, for which the following procedure has been found practicable. We dissolve 5 grms. of the sample in about 40 c.c. hydrochloric acid of specific gravity 1.124 (at 19° C.), placing the vessel upon the water-bath at a moderate heat. The solution is then evaporated to dryness at first on the water-bath and then in an air-bath at 120°. The dry residue is then covered with about 20 c.c. of the same hydrochloric acid, heated to boiling, and filtered off from the silica after dilution with a three-fold volume of hot water. The iron solution is concentrated in a porcelain capsule until vapours of hydrochloric acid escape, mixed with about 10 c.c. of concentrated hydrochloric acid, and

oxidised at the temperature of ebullition by means of from 2 to 2.5 c.c. nitric acid of specific gravity 1.4, added drop by drop. Finally the liquid is evaporated down to the consistence of a syrup or until a basic ferric chloride separates out. The solution thus prepared, about 10 c.c. is put in an apparatus of special construction, filled up to the volume of from 55—60 c.c. with hydrochloric acid of 1.124 (at 19°), and shaken out twice with ether. If relatively much copper and cobalt dissolve, both the first and the second ethereal solution of ferric chloride must be shaken out, each with 10 c.c. of hydrochloric acid of specific gravity 1.104, in order to remove the traces of copper and cobalt which have been dissolved in the ether along with the ferric chloride.

In preparing aluminiferous solutions of iron for shaking out with ether, particular care should be taken that the hydrochloric solution when concentrated is perfectly clear and contains no deposits of basic aluminium salts.—*Mitth. a. d. kgl. Techn. Versuchs Anstalten. Berlin und Chemiker Zeitung.*

ACTION OF SULPHUR IN PRESENCE OF WATER UPON THE SALTS FORMED BY THE POLYBASIC ACIDS.*

By J. B. SENDERENS.

I HAVE previously made known to the Society the results yielded by the action of sulphur in the presence of water upon the oxides of the salts formed by monobasic acids. Before explaining my new researches, I will make a slight correction concerning the oxides of nickel and cobalt. In the first moments of ebullition there are formed in both cases a sulphate and a hyposulphite, but as the operation continues, the hyposulphite gradually diminishes, in consequence of its formation into sulphate, so that at the end of the reaction the latter salt predominates exclusively in the liquid.

After this explanation, I come to the action of sulphur in presence of water upon the salts formed by the polybasic acids. Coloured reagents, and especially colorimetric observations, have shown us that the multiple acid functions superposed in the molecule of a polybasic acid may be—

(1) All strong; (2) all weak; (3) some strong and others moderate or weak.

1. Acids, the Acid Functions of which are Strong.

We consider as such the sulphuric, oxalic, and tartaric acids (bibasic); and the citric acid (tribasic).

Sulphur is without action upon the alkaline sulphates and oxalates in boiling solutions (whether acid or neutral), but it slightly decomposes the bibasic tartrate and the tribasic citrate, bringing their solutions to perfect neutrality. At the outset they have a slightly alkaline reaction with litmus and phenolphthalein.

Thus the action of sulphur upon the saline solutions in question indicates sulphuric, oxalic, and citric acids as having two strong acid functions. The same action attributes to tartaric acid a strong acid function and a medium acid function; and to citric acid two strong acid functions and a medium acid function.

2. Acids which have exclusively Weak Acid Functions.

Such are the carbonic and the boric acids. I have said in a previous communication that the solutions of the alkaline carbonates, whether neutral or acid, are completely decomposed by sulphur at the temperature of ebullition.

It is the same with the alkaline borates, acid and neutral. The analogy between these two kinds of salts extends to their metallic compounds. Thus the copper,

nickel, and lead borates are readily reduced by sulphur in presence of boiling water, as are also the corresponding carbonates. Boric acid is set free and the sulphur forms a sulphide and a sulphate with the bases.

3. Acids, the Acid Functions of which are some of them Strong and others Weak.

This case is presented by ortho-phosphoric acid, PO_4H_3 .

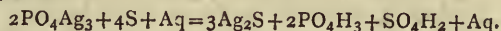
(a). *Alkaline Phosphates.*—M. Filhol and I have shown long ago that sulphur easily seizes in heat the third molecule of soda, yielding a polysulphide and a thiosulphate. I have since observed that there is an escape of sulphuretted hydrogen from the destruction of the polysulphide. The reaction does not stop at the disodium phosphate, and on continuing the operation the latter salt gives up to the sulphur half a molecule of soda.

(B). *Alkaline earthy Phosphates.*—The barium and calcium phosphates are decomposed by sulphur in presence of boiling water. Hydrogen sulphide escapes, and the liquid contains thiosulphate. This decomposition is extremely slow and does not go beyond the third molecule of the base. If we boil water with sulphur and the monacid or diacid alkaline-earthly phosphates, the latter salts do not undergo any change.

It results from these experiments that phosphoric acid with potassa or soda behaves like an acid possessing 1.5 of a strong acid function, but the baryta and lime as having 2 strong acid functions and 1 of a medium acid. Sulphur, in fact, which has no action upon sodium or barium sulphate has as little action upon sesquisodium phosphate or di-barium phosphate, whilst it decomposes the alkaline and alkaline-earthly carbonates and acetates to which it has been sought to assimilate the phosphate as far as the second molecule of the base is concerned.

The action of sulphur upon the metallic phosphates in presence of water shows us that the ortho-phosphoric acid has three strong acid functions.

(γ). *Metallic Phosphates.*—The tribasic silver phosphates, like the dibasic salt, are completely reduced by sulphur in presence of boiling water, according to the equation—



The three copper phosphates, $(\text{PO}_4)_2\text{Cu}_3$, $(\text{PO}_4)\text{HCu}$, $(\text{PO}_4)_2\text{H}_4\text{Cu}$, are likewise decomposed with the same reactions as the silver salts.

The lead, nickel, and cobalt phosphates remained unaffected in presence of sulphur and boiling water.

Thus, with reference to the metallic oxides, phosphoric acid possesses three strong acid functions, just as sulphuric acid has two with reference to the same oxides. In fact, copper and silver sulphates are reduced by sulphur in presence of water, as are also the phosphates of the same metals; but the tribasic phosphates of lead, nickel, and cobalt resist the action of sulphur like the corresponding sulphates.

(To be continued.)

NOTICES OF BOOKS.

Matriculation Chemistry: Chemistry of the Non-Metallic Elements and their Compounds. By TEMPLE ORME. London: Lawrence and Bullen. 1892. 12mo., pp. 240.

This little book raises anew the painful question—By what process do the authors of such treatises persuade themselves that there is still need for chemical manuals "intended for beginners"?

We see nothing objectionable in the work before us, but as little can we discover its *raison d'être*. Surely, pending some capital discovery, such as the decomposition of one of the reputed elements, beginners might find

* *Bulletin de la Soc. Chimique.*

their wants met by some one of the multitude of existing treatises.

The Practical Polish and Varnish Maker. A Treatise containing 750 Practical Receipts and Formulæ for the Manufacture of Polishes, Lacquers, Varnishes, and Japans of all Kinds, for Workers in Wood and Metal, and Directions for Using. By H. C. STANDAGE (Author of "The Artists' Manual of Pigments," &c.). London: E. and F. Spon. New York: Spon and Chamberlain. Small 8vo., pp. 260.

THIS book consists almost entirely of recipes, the value of which can only be decided on by actual use. The author informs us that many of the formulæ given have been practically tested by him, and that the sources from which his information has been drawn are perfectly trustworthy. He states the precise proportions of the ingredients to be used, and gives full instructions on the manner of putting them together. Practical directions have also been given for the use of the various varnishes, polishes, &c.

As the work is intended mainly for amateurs, it treats of the so-called spirit varnishes alone. The oil varnishes have not been included in the author's plan, as their preparation requires special and costly appliances.

The first chapter of the book gives an account of the materials used in making up varnishes; then follow directions for filtering and bleaching varnishes and lacquers, and the remainder of the book is devoted to practical recipes.

The book, so far as we can judge, seems calculated to be very useful.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I observe in the CHEMICAL NEWS (p. 172) a letter from Mr. G. H. Robertson, Registrar of the Institute of Chemistry. Kindly permit me to make a few observations upon the action of the Institute in the case he has mentioned.

A certain appointment was vacant, legally and morally, for which I made application in writing. In the course of a few days, I received from Mr. Groves, then Secretary, a letter stating that a Fellow of the Institute had lodged a complaint with the Censors against me of unprofessional conduct, which, as stated by the Censors, consisted in "that I had applied for an appointment which another Fellow held." I never applied for any appointment held by any Fellow; I have never applied for any appointment that was not legally vacant, and the appointment I did apply for was legally filled up some months afterwards. The Council, taking advantage of the powers contained in their Charter, and acting under the influence of Teutonic terror, removed my name from the Register upon an absolutely false charge for an offence I did not commit.

The action against the Institute was raised so as to enable me to obtain possession of the contents of a libellous letter written to the President, and it must become apparent to the novice that a "body corporate," possessed of practically unlimited powers over the actions of its members, must have sinned grievously and been hard pressed when they agreed to pay their own costs—costs amounting to about £500—if I withdrew the case. They do not stop there; but they go further, and express through a most eminent Q. C. "that they have no charge against my professional capabilities or personal character, but of the view of the Council on the professional conduct of the plaintiff on one occasion." That one occasion is

the charge stated above, and I utterly defy them to substantiate or repeat this false charge, under cover of which my name was removed from the Register.

If my public and private character merits such high merit as they have acknowledged they do, Emeritus Fellow will in the future distinguish between past and present Fellows who still hold Certificates of Membership, although their names do not appear upon their Register. All things must have a beginning, as the Institute had. It is a young Society at variance with itself, and their actions have created the title of Emeritus Fellow.—I am &c.,

WILLIAM JOHNSTONE,
Emeritus Fellow of the Institute
of Chemistry.

London, October 4, 1892.

METHODS FOR THE DETERMINATION OF ORGANIC MATTER IN DRINKING WATER.

To the Editor of the Chemical News.

SIR,—In view of the very strongly worded assertions of articles on this subject which have recently appeared in the CHEMICAL NEWS (vol. lxxvi., pp. 102 and 111), it may be allowable to direct attention to an extensive report which I prepared several years ago for the U.S. National Board of Health, giving the results of a careful study of the chief methods in use, and numerous analyses in which these methods were tested by simultaneous application under similar conditions to carefully selected samples of water of known character—some good and wholesome; some held, on good medical authority, to have actually produced disease; some artificially polluted with known forms of manufacturing refuse and products of disease—the history of each sample being in every case unknown to the analyst, and the sole object being an absolutely fair and impartial contrast between the methods employed.

The original paper forms a part of the Annual Report of the U.S. National Board of Health for 1882 to the Secretary of the Treasury, pp. 189 to 353, with tables; and an abstract, or, rather, a preliminary report, appeared in the CHEMICAL NEWS (vol. xlvii., pp. 63, 72, 90, 101, 108; and vol. xlviii., pp. 218 and 232).—I am, &c.,

J. W. MALLET.

ON THE ORGANISATION OF SCIENCE.

To the Editor of the Chemical News.

SIR,—I am exceedingly sorry that in speaking of the very timely pamphlet by "A Free Lance" I did not express myself in a manner incapable of being misunderstood. I referred, of course, to what I and not a few others regard as the main defect of the Provincial Societies, viz., the unhappy attempt to combine the cultivation of science and of literature in one and the same organisation. The consequence is that literature obtains the lion's share, both of time at the Society's meetings, and of space in the printed Transactions. Science is even at times grossly insulted.—I am, &c.,

YOUR REVIEWER.

"Anicol."—F. Goldmann.—Under this name a "proprietary article" has been introduced to the world as the "sovereignest thing" for febrile affections. It has been unmasked, and is found to consist of 75 per cent antifebrine, 17.5 per cent sodium bicarbonate, and 7.5 per cent tartaric acid! It is modestly offered at about six times the price of antifebrine.—*Chemiker Zeitung and Pharm. Rundschau.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 12, September 19, 1892.

The Action of Bromine in Presence of Aluminium Bromide upon Carbides with Cyclic Chains.—W. Markownikoff.—The author proposes the following rule. The action of bromine upon the naphthenes in presence of aluminium bromide at the ordinary temperature bears principally upon the atoms of hydrogen of the cyclic chain, transforming it into a benzene nucleus in which all the atoms of hydrogen are replaced by bromine whilst the lateral chains remain intact. But the most simple naphthene, hexahydrobenzene, C_6H_{12} , presents a remarkable exception, since it does not yield hexabromobenzene but another bromine product.

The Rotatory Power of Fibroïne.—Leo Vignon.—The substance precipitated from hydrochloric solutions of fibroïne by alcohol has the same power of absorbing colouring-matters as ungummed silk.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 13.

Preparation and Purification of the Propylamines.—F. Chancel.—We may easily prepare the three propylamines by the action of aqueous ammonia upon propyl chloride if we take sufficient alcohol to dissolve the whole. The dry bases may be accurately separated by successive rectifications, and to complete their purification we isolate the primary base in the state of dipropylamide or of acid oxalate, the secondary base in the state of an acid oxalate, and the tertiary base as a picrate.

The Action of Oxalic Ether upon Aqueous Monopropylamine. Monopropylloxamic Acid.—F. Chancel.—Monopropylloxamic acid has the composition expressed by the formula $C_5H_9NO_2$. The author has obtained and examined its calcium and barium salts.

Propylamidoacetic Acid.—F. Chancel.—This compound is obtained by the action of monopropylamine upon ethylbromacetate. Its composition is $C_6H_{14}NO_2$. The author describes its hydrochlorate, its platinochlorate ($C_5H_{12}NO_2 \cdot PtCl_6 + H_2O$), its chloraurate, and the copper propylamidoacetate.

Dibromogallac Acid and the Dibromogallates.—Alex. Bietrix.—This acid ($C_6Br_2(OH)_3COOH$), forms white or slightly yellowish needles, sparingly soluble in cold water, very soluble in boiling water, alcohol, and ether. It takes a rose-colour in contact with alkalis; the ethereal solution takes an indigo-blue colour with baryta-water, which turns red on the addition of water. The author has prepared and determined the ammonium, sodium, zinc, lead, barium, quinine, and strychnine dibromogallates.

Researches on Persulphuric Acid and its Salts.—M. Berthelot.—The author has studied these bodies chiefly from a thermo-chemical point of view, determining the solution, neutralisation, and formation-heats.

Formation-Heat of Hydrazine and of Azothydric Acid.—This paper consists of a series of thermochemical determinations.

The Combustion- and Formation-Heats of Alcohol and of Formic and Acetic Acids.—MM. Berthelot and Matignon.—The character of this paper appears from the title.

Combustion- and Formation-Heats of the Nitrobenzenes.—MM. Berthelot and Matignon.—A thermo-

chemical study of dinitrobenzene in its ortho, meta, and para types; and of trinitrobenzene, symmetric and dissymmetric.

Thermo-chemical Data.—MM. Berthelot and Matignon.—Determination of the solution-heat of hydroxylamine, and of the neutralisation-heat of hippuric acid.

A Contribution to the History of the Mechanical Arts and of Artillery towards the End of the Middle Ages.—M. Berthelot.—Mention of a memoir published by M. Berthelot in the December number of the *Annales de Chimie et de Physique*.

New Method of Organic Analysis.—M. Berthelot.—The method consists in burning the compound in the calorimetric bomb in oxygen compressed at twenty-five atmospheres. The combustion is total and instantaneous. The sulphur in organic matters may be completely determined by adding beforehand 10 c.c. of water. The sulphur remains in the water in the form of sulphuric acid. Phosphorus may be determined in a similar manner. Chlorine may also be determined by introducing previously into the bomb an aqueous solution of arsenious acid. For compounds very rich in chlorine the combustion is effected with the addition of a suitable dose of camphor.

On Nickel-Carbonyl.—M. Berthelot.—Carbon monoxide has the property of combining in the cold with nickel, forming special compounds analogous to the compound metallic radicles. Carbon monoxide behaves in this respect like the hydrocarbons.

Oxidation of Nickel-Carbonyl.—M. Berthelot.—The product of the analysis of the slow oxidation of this compound is whitish in small quantities, but it appears green in masses. Its composition is $C_2O_3Ni_3 \cdot 10H_2O$. It is the oxide of a complex radicle analogous to the croconic and rhodozenic acid.

On Ferro-Carbonyl.—M. Berthelot.—In order to combine with carbon monoxide the iron should be reduced with hydrogen slowly and at the lowest possible temperature, then washed and carefully dried. The reaction of carbon monoxide upon iron in this state takes place at about 45° . The combination of iron with carbon monoxide plays doubtless a part in certain reactions observed in metallurgy, such as the precipitation of the carbon of carbon monoxide in contact with iron (observed by Gruner), the formation of gaseous bubbles in softened iron (observed by Cailletet), &c.

Some New Observations on the Determination of Sulphur in Vegetable Soil, and the Nature of the Compounds which it Forms.—MM. Berthelot and Matignon.—Sulphur exists in vegetable soils and in plants in the state of special organic principles, the proportion of which often far exceeds that of the sulphates also present. The organic compounds contained in the soil are very stable.

Silica in Plants.—M. Berthelot and G. André.—The authors trace the presence of silica in wheat at different stages of its growth.

Researches on the Humic Substances.—M. Berthelot and G. André.—Humic anhydride shows at once the properties of the acid anhydrides and the alcoholic anhydrides, and is comparable to the lactones.

Calorimetric Researches on Humic Acid derived from Sugar.—MM. Berthelot and André.—Humic acid is a polybasic acid capable of losing a part of its water of hydration by simple desiccation, and even in water at the ordinary temperature by reason of a true dissociation.

The Spontaneous Oxidation of Humic Acid and Vegetable Mould.—M. Berthelot and G. André.—Already inserted.

The Fermentation of Blood.—M. Berthelot and G. André.—The products of the fermentation are carbonic acid, free from hydrogen and nitrogen, ammonia, volatile fatty acids, fixed nitrogenous principles.

MISCELLANEOUS.

Specific Determination of Xylose.—G. Bertrand.—If there is only a very small quantity of xylose available, e.g., 0.1 grm., its nature may be determined by proceeding as follows. The sample, supposed to be crude syrup of xylose, is left to itself. If crystallisation is slow in appearing the syrup, with the aid of heat, is stirred up in absolute alcohol. After sufficient settling the cold alcoholic solution is decanted off to separate it from the deposit formed and evaporated to a syrupy consistence; the crystallisation is then almost always easy. The crystals are then examined and drained in a porous plate. They are then stirred up in alcohol and drained anew, repeating this operation if needful. It is now necessary to ascertain if we have to do with xylose. For this purpose we heat a few m.grms. with a little hydrochloric acid and a trace of orcin. If the mixture takes a violet-blue colour we are in presence of a pentose, but if the colour is a reddish-orange we have one of the glycoses in C₆. It is only necessary to distinguish xylose from arabinose by means of cadmium xylonobromide.—*Bull. Soc. Chim. de Paris*, Series 3, No. 14.

The Swiss Scientific Association.—The seventy-fifth Congress of this body took place at Bâle from September 4th to 7th. Prof. Forel discussed the "Thermics" of lakes, with especial reference to the lake of Geneva. He considers lakes as storehouses of heat, and consequently of the highest physical and biological importance. Prof. C. Schmied discoursed on the metamorphosis of the Alpine rocks, exhibiting splendid thin slides of different rocks prepared in polarised light. Prof. Noelting communicated the results which he had recently obtained whilst prosecuting his researches on the triphenylmethane colouring-matters. Goldschmidt read a paper on the aldioximes, and Schar treated on the influence of hydrocyanic acid upon certain ferments, and on the poisonous principle of the seeds of *Abrus precatorius*. Wislicenus discussed the conversion of fumaric acid into maleic acid in presence of hydrochloric acid. A communication by Professor Thiescher on the chemistry of the spermatozoa excited no small sensation. Prof. Raoul Pidet delivered an address to the Association on the part of low temperatures in contemporary Science. He showed that at extremely low temperatures the reactions of bodies, generally known as "affinity," came to an end. The Association will meet next year at Lausanne.—*Chemiker Zeitung*.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Monazite.—We will be greatly obliged for the name of any technical or scientific books giving information about monazite, where it is found, and for what use it is employed.—RICHARD BAKER, SON, AND CO.

Detection of Oils.—Would any correspondent be kind enough to inform me how to separate, or at least detect, castor oil, rape seed oil, cotton seed oil, olive oil, linseed oil, from or in a paste containing vaseline; and each of the above oils in succession (1) in their simple form, (2) when they are saponified.—X. Y. Z.

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THE CHEMICAL NEWS.

Vol. LXVI., No. 1716.

NOTE ON

THE CAUSE OF THE COLOUR OF MILK.

By SIR CHARLES A. CAMERON.

IN the third volume (recently published) of the new edition of Watts' "Dictionary of Chemistry," the subject of the constitution of milk globules is discussed at some length. There are several authorities quoted in opposition to Henle's statement that the fat globules have albuminous envelopes. I would like to state that before any of the authorities quoted had contravened Henle's statement I had pointed out in a paper (*Scientific Proceedings of the Royal Dublin Society*, 1875), read before the Royal Dublin Society, 18th January, 1875, that free fat globules were exceedingly numerous in milk. I also stated that the colour of milk was due to the large number of casein films suspended in it, and not to an emulsion of fats and albumenoids.

I succeeded in extracting from milk all its fats save a mere trace, and yet the former remained a perfectly white opaque fluid. Butter-milk, which contains from 0.3 to 0.6 per cent of fats only, is whiter than milk diluted with its own weight of water, yet the latter is three times as rich in fats.

ON A NEW BLOWPIPE ARRANGEMENT.*

By WILLIAM HAMLET, F.I.C.,
Government Analyst, N.S.W.

THE blowpipe consists of the usual fine platinum jet fastened to a brass tube jointed on to a sliding rod inserted into a brass stand, by which means the jet may be inclined to any desired angle.

The air-blast is urged by means of one of the ordinary caoutchouc spray-producing balls obtainable at any pharmacy; these balls are attached to a piece of capillary lead-glass tube, over one end of which a piece of oiled silk is tightly tied, thus forming a valve that only opens inwards and prevents any back flow of air. The valve is passed through a cork and inserted into the inlet of an air-tight chamber made of tin plate and measuring 10×8×1 inches; this air chamber is placed out of sight by screwing on to the underside of the blowpipe table, which measures 18×10 inches, and stands on four legs 1½ inches high.

To the left of the front is an upright frame made to hold a sheet of glass six inches square; into the groove made in the frame, ruby, violet, green, and colourless glasses may be inserted as wanted. At a point two inches from the left edge is a brass rod six inches high which serves to hold a glass tube bearing a fine platinum wire for flame reactions.

The lamp may be any one of the many varieties of paraffin or grease lamps having a flat wick. In my own case I employ the lamp found in Letcher's blowpipe outfit, using solid paraffin as fuel. On the extreme left, just midway across the board, is a brass plate 2×1 inches, hard soldered on to a universal joint (not shown in the photograph, because I at first used merely a slip of wood hinged to a block). This forms a convenient support when protected by a piece of asbestos millboard for charcoal pellets or cubes, as well as for plaster slabs and aluminium plates. The upright prism of porcelain is used for cupelling.

On the right is embedded into the table a flat steel anvil and an agate mortar. Such a blowpipe becomes a valuable adjunct to the laboratory equipment, and instead of the blowpipe being despised and consigned to the drawer or box of odds and ends it finds a useful place on the working bench. With such a piece of apparatus one can get a very clearly defined reduction or oxidation flame, and when the jet slopes down on to the wick at the proper angle, it is easy to produce a flame four inches long and so steady that I have actually cupelled off a lead button as perfectly as it could have been done in the muffle. Such a thing is sometimes stated in books, but I never saw it accomplished until I actually did it myself with the apparatus I now describe.

Using the flame colouration and a blue screen, it is quite possible to see the potassium flame amid the abundance of sodium salts in urine. Conversely, the presence of sodium salts in potassium compounds may be recognised by using the green tinted screen.

Altogether it is the most efficient and the most easily handled blowpipe arrangement I know of, and I made good use of it during my recent visit to the Broken Hill Silver Lead Mines.

With the steady flame obtained, Von Kobell's reaction for bismuth compounds gives most brilliant results on a slab of plaster of Paris, and with dry thiosulphate all the reactions may be instantly obtained in the dry way that are usually given in the wet way with sulphuretted hydrogen.

THE ANALYSIS OF THE CAVENDISH BANANA (*MUSCA CAVENDISHII*) IN RELATION TO ITS VALUE AS A FOOD.*

By W. M. DOHERTY,
Assistant Government Analyst, New South Wales.

THE value of the banana as a perfect food has been frequently extolled, but so far as I can learn no analysis of the fruit has yet been published, and nothing is known of its food value beyond general practical experience. To supply a conspicuous gap on the list of fruits which have been submitted to investigation this analysis has been undertaken.

The Cavendish, or, as it is sometimes called, Fiji variety, has been selected because of its enormous consumption in Australia, where it has almost completely dislodged all the other kinds. This banana is the product of a plant which grows only to a height of about six feet, and it has therefore received the appellation "dwarf." Its original home was China, from which country it was brought to England by the Duke of Devonshire (hence the name Cavendish), and cultivated by him in the celebrated Chatsworth Gardens. From England it was brought to Fiji by a party of missionaries, thence finding its way to Australia. It is now grown to a considerable extent in Queensland, and will thrive well in the northern parts of New South Wales, especially in the Tweed River district.

The banana has been described as "the produce of one of the most splendid plants of the world. Underground there is a substantial root stock of long duration, from which rise stems, branchless, like those of palms, and carrying upon the summit half a dozen superb leaves of great size, of a rich lucid green, and which arch away from it on their long petioles, magnificently. The veining of the leaves is of a very rare and elegant kind, which has been fittingly called featherlike; innumerable lateral veins flowing from the midrib in a curvilinear manner towards the margin. The stem is composed in reality of no more than the sheathing and closely compacted bases of the older petioles, in the heart of which, near the

* Exhibited before the Royal Society, N.S.W.

* Australasian Association for the Advancement of Science, Hobart, 1892, Section B.

ground, the flower bud is generated. This in due time develops itself from among the youngest leaves as a huge pendulous raceme, constituted of crimson bracts, which protect innumerable though rather trifling flowers, followed again in due time by the well-known fruits—cylindrical, six or eight inches long, an inch or more in diameter, slightly curved, and when ripe pale yellow. The clusters of fruit are often four feet long, and weigh from twelve to sixty or eighty pounds. In the tropics it is said that two plants will grow anywhere—the castor oil and the banana. This is not only true, but it may be added with equal justice that no plant furnishes man spontaneously with supplies so vast of a pleasant and nourishing food. In countries where the mean heat of the year is never lower than 75° F. the banana is the bread of the poor, and this all the year round, literally yielding fruit every month."

The analysis was made upon picked specimens, divested of the skin.

Composition in 100 Parts.

Water	75.71
Albumenoids	1.71
Starch	5.90
Sugar	3.00
Carbonaceous matter (non-nitrogenous) ..	11.24
Woody fibre.. .. .	1.74
Ash	0.71

Composition of the Ash.

Potash (K ₂ O)	55.10
Soda (Na ₂ O)	12.00
Lime (CaO)	1.61
Magnesia (MgO)	5.41
Phosphoric acid (P ₂ O ₅)	7.70
Sulphuric acid (SO ₃)	1.80
Carbonic acid (CO ₂)	12.00
Chlorine (Cl)	1.10
Oxide of iron (Fe ₂ O ₃)	0.48
Silica (SiO ₂)	1.96
Oxide of manganese (MnO ₂)	0.15
Loss, &c.	0.69

100.00

Composition of the fruit, and percentage of mineral constituents, calculated dry:—

In 100 Parts.

Albumenoids	7.05
Starch	24.78
Sugar	12.35
Carbonaceous matter (non-nitrogenous) ..	47.05
Woody fibre.. .. .	7.26
Potash (K ₂ O)	1.610
Soda (Na ₂ O)	0.340
Lime (CaO)	0.047
Magnesia (MgO)	0.158
Phosphoric acid (P ₂ O ₅)	0.224
Sulphuric acid (SO ₃)	0.052
Carbonic acid (CO ₂)	0.340
Chlorine (Cl)	0.032
Oxide of iron (Fe ₂ O ₃)	0.014
Silica (SiO ₂)	0.057
Oxide of manganese (MnO ₂)	0.004

= Ash, 2.92

From the small quantity of albumenoids or flesh-forming substances present in the banana, it cannot be considered by itself a convenient food, or even sufficiently nutritious for all the requirements of man. Under normal conditions the average man requires daily 4.2 ounces of albumenoids. To obtain this quantity from the banana fifteen pounds weight of the fruit would have to be consumed—a quantity altogether excessive and decidedly inconvenient, containing no less than nine pints, or over a gallon, of water.

In nutritive properties the Cavendish banana bears a

resemblance to the potato, as will be seen from the comparison following. It may be described as a very unevenly balanced food, not suited alone for the diet of man, but an excellent and wholesome addition to a diet rich in nitrogenous substances.

Comparison Analysis.

	Cavendish banana.	Potato.
Water	75.71	75.77
Albumenoids	1.71	1.79
Total carbonaceous matter (non-nitrogenous)	20.13	20.72
Woody fibre	1.74	0.75
Ash	0.71	0.97

VOLATILE FATTY ACIDS OF BUTTER.

By WILLIAM JOHNSTONE.

CONTINUING my research upon the composition of butter-fat, the following experiments are worth recording. A genuine butter yielding 85.6 per cent of insoluble fatty acids was operated upon, 5.433 grms. being taken and saponified in the usual manner for a Reichert-Wollny estimation of the volatile fatty acids.

During the distillation a quantity of solid volatile fatty acid collected in the condenser tube amounting to 0.273 gm., the iodine absorption of which was ascertained and gave the following results:—

Iodine solution taken	30.0 c.c.
Na ₂ S ₂ O ₃ equivalent to iodine taken	31.6 "
Na ₂ S ₂ O ₃ equal to oxidised remaining iodine ..	27.8 "

Na₂S₂O₃ equivalent to iodine absorbed .. 3.8

1 c.c. of Na₂S₂O₃ = 0.01203 gm. iodine.

$$\frac{3.8 \times 0.01203 \times 100}{0.273} = 16.74 \text{ per cent iodine absorbed.}$$

The distillation was continued upon the addition of more water until the flask broke, a further quantity of solid volatile acid having been obtained amounting to 0.332 gm., giving a total of 0.506 gm., equal to 9.31 per cent of solid volatile insoluble fatty acid. When the retort broke the fatty acids were distilling as rapidly as at the commencement of the experiment.

The 0.332 gm. was converted into a barium salt and extracted with ether, of which 0.355 gm. were taken, and dried at 100° C. for two hours, losing a m. gm. at 130° C. which, when ignited with sulphuric acid, gave 0.136 gm. BaSO₄:—

$$\frac{0.136 \times 100}{355} = 38.31 \text{ per cent BaSO}_4.$$

A further portion of this solid volatile fatty acid was converted into a lead salt, washed with alcohol, and then thoroughly extracted with ether; the lead salt insoluble in ether was decomposed, and the melting-point of the fatty acid taken, 53.2° C.; it was now dissolved in alcohol and made into an ammonia soap, and then precipitated with nitrate of silver, 0.456 gm. of the silver salt giving 0.1465 gm. of Ag equal to 32.12 per cent of myristic acid requiring by theory 32.23 per cent of silver; consequently the barium salt probably consisted of—

(C ₁₈ H ₃₃ O ₂) ₂ Ba ..	17.78	5.92 per cent BaSO ₄ .
(C ₁₄ H ₂₇ O ₂) ₂ Ba ..	82.22	32.41 " "

100.00 38.33

BaSO₄ found .. 38.31 per cent.

Or the solid fatty acids which collect in the condenser consists of—

18.6 per cent of pseudo-oleic acid.
81.4 " " myristic acid.

The volatile soluble fatty acids of this butter were converted into a barium salt and yielded in duplicate 73.57 and 73.61 per cent of barium sulphate, 1.8336 and 2.0464 grms. of the barium salt having been taken respectively for the estimation.

Butyric acid requires by theory 74.92 per cent BaSO_4 . The remainder of the soluble volatile fatty acid was then heated with bichromate of potash and sulphuric acid attached to upright condenser for two hours, the volatile acid then distilled off and converted into barium salt, 1.1946 grm. of which gave 74.38 per cent BaSO_4 .

SIXTH REPORT OF THE COMMITTEE*

APPOINTED FOR THE PURPOSE OF INVESTIGATING
ISOMERIC NAPHTHALENE DERIVATIVES.

It was stated in the last report that Mr. Rossiter and the writer had devoted much time to the study of the dibromonaphthalenes, but that the results were not sufficiently complete to render their publication desirable; an account of the work contemplated in this passage was communicated to the Chemical Society late in the year (*cf. C. S. Proceedings*, 1891, p. 182).

In this communication, data were given which suffice to characterise and differentiate five of the isomeric dibromonaphthalenes, *i.e.*, the 1:4, 1:4', 1:3, 1:2' and 1:3' modifications. The action of bromine on α - and β -dibromonaphthalene was also described, and the nature of the complex product formed on *di*-brominating naphthalene, which has occupied the attention of so many observers, was finally determined, it being shown to consist of 1:4 dibromonaphthalene (m. p. 82–83°) mixed with the 1:4' isomeride (m. p. 132°).

When naphthalene is dibrominated, 1:4 dibromonaphthalene is the major product, so much so that this modification crystallises out in an almost pure state from the solution of the crude product in alcohol. It has been stated by Darmstaedter and Wichelhaus that when naphthalene- α -sulphonic acid is brominated, a product is obtained which on crystallisation from alcohol first affords 1:4' dibromonaphthalene, the remainder of the product melting at 68–70°, and resembling that obtained from naphthalene. It therefore seemed probable that whereas naphthalene yields chiefly 1:4 dibromonaphthalene, the α -sulphonic acid yields chiefly the 1:4' derivative, and that consequently the *acid*-radicle exercises a marked influence in determining the entrance of bromine into the unsubstituted nucleus (*cf. Report* for 1886), an influence much greater than that of bromine towards sulphuric acid, as bromonaphthalene yields little but the 1:4 acid when sulphonated. Darmstaedter and Wichelhaus's experiments have been repeated by the writer, and the accuracy of this conclusion confirmed; a very considerable amount of 1:4' bromosulphonic acid is formed on brominating naphthalene-sulphonic acid, 1:4 dibromonaphthalene being quite a minor product.

On comparing the dibromo-products obtained from naphthalene with the dichloro-products, an unusual divergence is apparent; there can be no doubt, however, that this is attributable to the extreme instability of bromine addition compounds of naphthalene. The dichloronaphthalenes are, in fact, products of the withdrawal of 2HCl from the tetrachloride, while the dibromonaphthalenes are products of the action of bromine on bromonaphthalene, and hence it is that the 1:3 modification, which is the chief product of chlorination, is absent from the product of bromination. When the conditions are similar the difference in behaviour of naphthalene towards chlorine and bromine is of the ordinary character,

and such as was to be expected; thus when α -chloronaphthalene is chlorinated by means of SO_2Cl_2 at such a temperature (100–180°) as to prevent the persistence of an addition compound, it yields pure 1:4 dichloronaphthalene and no trace of the 1:3 isomeride, which is the principal product of the hydrolysis of naphthalene tetrachloride. β -Chloronaphthalene in like manner yields a mixture of the 1:2 and 1:2' derivatives. The results of a series of experiments on the formation of chlorinated naphthalenes at high temperatures by means of SO_2Cl_2 and similar chlorinating agents which the writer and Dr. Wynne are engaged in carrying out will be given on a subsequent occasion; they desire, however, here to recognise the assistance which they have received from Mr. Jenks.

Finally, it may be mentioned that Mr. Rossiter and the writer, having repeated Meldola's experiments on the bromonitronaphthylamines, have been led to interpret this author's results in a manner somewhat different from that originally adopted by him, but in accordance with the results of more modern enquiries (*cf. C. S. Proceedings*, 1891, p. 186; Meldola, *C. S. Trans.*, 1892, p. 766).

A comprehensive survey of the very numerous recorded facts shows that "the laws of substitution" in the naphthalene series are in the main easy to decipher, and pervaded by a few very simple principles. The writer and Dr. Wynne hope during the coming year to discuss these in a comprehensive memoir, dealing with the investigation which they have conjointly carried on now during over six years. It is perhaps not undesirable to state that no single fact has yet been recorded serving to support the view advocated by Claus, that the structure of naphthalene is unsymmetrical. Whatever its exact inner structure may be, the two nuclei of naphthalene must be represented alike.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Continued from p. 177).

THESE results, in the case of acid of the concentration used, would seem to indicate that the phenomenon is not entirely one of solution, but partly also of reversible chemical changes, the difference in their relative intensities being greatest at or about 32°, and at least 52°, a temperature at which nitrous acid by itself would be very rapidly decomposed. These results were also confirmed by experiments conducted with a sample of acid of half the concentration of that used above.

Concentration of nitric acid = 0.1279 grm.

SERIES VII.—Temperature, 22.5°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.1257	0.0124	89.79 : 10.21
4	0.1276	0.0136	90.37 : 9.63

SERIES VIII.—Temperature, 32°.

3½	0.1203	0.0137	89.78 : 10.22
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SERIES IX.—Temperature, 42°.

3	0.1185	0.0114	91.22 : 8.78
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SERIES X.—Temperature, 52°.

3	0.1274	0.0088	93.54 : 6.46
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In these sets of experiments, also, the amount of nitrous acid formed increases up to a temperature of 32°, and from this point again decreases. Further, from compari-

* Consisting of Professor W. A. Tilden and Professor H. E. Armstrong (Secretary). (Drawn up by Professor Armstrong). Read before the British Association, Edinburgh Meeting, 1892, Section B.

* A Paper read before the Royal Society, June 2, 1892.

son of results obtained with the two samples of acid at the same temperature it is evident the percentage ratio of nitrous acid is *increased with decrease of concentration*. To confirm this a further series of experiments were conducted with an acid of one-fourth of the concentration of that used in the first set.

Concentration of acid = 0.0655 grm. in 1 c.c.

SERIES XI.—Temperature, 22.5°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
4½	0.0662	0.0097	87.22 : 12.78
2	0.0661	0.0088	88.25 : 11.75

SERIES XII.—Temperature, 32°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.0624	0.0097	86.55 : 13.45
2	0.0634	0.0105	85.79 : 14.21

SERIES XIII.—Temperature, 42°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.0630	0.0081	88.61 : 11.39

SERIES XIV.—Temperature, 52°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.0652	0.0062	91.31 : 8.69

The results given in the four tables above are perfectly in accordance with those of the preceding series, the maximum value for the amount of nitrous acid being as before, at a temperature of 32°; they also show that with decrease of concentration the percentage ratio of nitrous acid is increased, though its total amount is decreased. Experiments were then conducted with acids of greater concentration, the results of which are given below.

Concentration of acid = 0.3457 grm. in 1 c.c.

SERIES XVI.—Temperature, 22°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.3254	0.0268	92.39 : 7.61

SERIES XVII.—Temperature, 32°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.3253	0.0212	93.88 : 6.12

SERIES XVIII.—Temperature, 42°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.3080	0.0173	94.68 : 5.32

Concentration of acid = 0.6338 grm. in 1 c.c.

SERIES XIX.—Temperature, 22.5°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3	0.5910	0.0397	93.74 : 6.26
3 (expt. repeated.)	0.5791	0.0408	93.42 : 6.58

SERIES XX.—Temperature, 32°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
3½	0.5306	0.0295	94.74 : 5.26

The liquids obtained in the experiments detailed above were of a *blue* tint, but it was also observed that in the case of the more concentrated acids red fumes were evolved to a slight extent, thus showing under these conditions a more complex reaction than the simple reversible change given above. It is also to be noticed that the sum of the quantities of nitrous and nitric acids found are less than the quantity of nitric acid originally taken, thus showing that some unaccounted for destruction of the acid had taken place. In a set of experiments with more concentrated acids the evolution of fumes and the destruction of the acid were further noticeable.

Concentration of acid = 1.089 grm. in 1 c.c.

SERIES XXI.—Temperature, 22.3°.

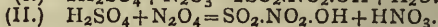
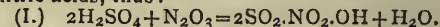
Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
1½	0.8704	0.0632	93.25 : 6.75
2 (expt. repeated.)	0.8700	0.0664	92.91 : 7.09

SERIES XXII.—Temperature, 27°.

Time. Hours.	Nitric acid in 1 c.c. Grm.	Nitrous acid in 1 c.c. Grm.	Percentage ratio.
1½	0.7009	0.0391	94.72 : 5.29

In the above series of experiments, when the nitric oxide gas was first passed in, a yellow colour was produced, but this speedily changed into a deep *green* tint. It thus appeared that nitrogen peroxide was at first produced and this was converted possibly by the nitric oxide and possibly, also, by the water present, into the green acid which certain writers have considered to have the composition $\text{N}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$; such an acid, however, would contain nearly 50 per cent of nitrous acid.

After most of the experimental work above detailed had been performed, a paper appeared by F. Marchlewski (*Ber. Deut. Chem. Gesell.*, vol. xxiv., p. 3271), entitled "Zum Kenntniss der verschiedenen Färbungen der Salpetersäure," in which the author describes various experiments upon the reaction between nitric oxide and nitric acid. The main object of the paper was to determine the composition of the various coloured liquids produced when nitric oxide, nitrous fumes, and nitrogen peroxide are passed into nitric acid of different concentration. The method employed consisted in preparing such liquids and then decolourising them by a current of carbonic anhydride; the gases evolved were passed into sulphuric acid and the solution subjected to analysis. The process is based upon the observations of Lunge that nitrous fumes give under these conditions nitrosyl sulphuric acid, while nitrogen peroxide gives a mixture of nitrosyl sulphuric and nitric acids, thus:—



It might appear open to question whether the composition of these liquids can be ascertained by this indirect method, and whether a liquid apparently decolourised contains nothing but the residual nitric acid (more or less diluted) of the operation. My own experience has shown that it is extremely difficult to remove the last traces of the yellow colour from the more concentrated acids; though, on the other hand, it must be allowed that the method of analysis adopted in the text would not distinguish between nitrous acid, on the one hand, and nitrogen peroxide on the other, the latter of which would appear in the course of analysis as an equimolecular mixture of nitrous and nitric acids. These remarks would, however, apply probably only to the two last series of experiments. Marchlewski gives no observations of time, temperature, or degree of humidity of gases, whether oxides of nitrogen or carbonic anhydride, nor a single control analysis of the residual nitric acid. Some proof is given that the difference between the *green* and *blue* acids is dependent upon not only the water present, but also upon the dissolved nitric oxide. Marchlewski seems to be quite unaware of the observations of Péligot,* made nearly forty years ago, upon the same subject.

Certain experiments were made upon the action of dry nitric oxide upon nearly anhydrous nitric acid (specific gravity $7/7^\circ = 1.5326$), the preparation of which has been described in a previous section. The air was driven out of the apparatus by a current of carbonic acid dried by passage through a wash-bottle containing concentrated sulphuric acid, and then through three drying tubes filled with pumice and phosphorus pentoxide. The nitric acid was contained in the Geissler's bulbs as before (kept at a temperature of 11°), and subsequent to them was another wash-bottle of sulphuric acid to prevent the access of moisture by backward diffusion.

On passage of the nitric oxide gas, the portion of acid in the first bulb was turned a yellow tint, which gradually deepened to an orange-red; when about a litre of

* *Ann. Chim. Phys.*, [III.], vol. ii., p. 58. The remarks of Péligot seem worth transcribing, as having possibly fallen into undesired oblivion: "Comme l'acide azoteux pur paraît être bleu tandis que l'acide azotique et l'acide hypoazotique mélangés sont jaunes on obtient par cette action de l'eau" (viz., upon nitrogen peroxides) "selon les proportions employées les différents nuances de vert et de bleu . . . qui se développent également par l'action du bioxyde d'azote sur l'acide azotique à différents degrés de densité. Le produit vert . . . se forme aussi par le contact du bioxyde d'azote avec l'acide hypoazotique, et sa production pouvait être tout à fait indépendante de l'eau" (as shown by experiment).

the gas had been driven through a red oil appeared floating upon the surface of the acid, and a few minutes after the red oil turned a green tint, and for some time there were two distinct liquids of different densities in the bulb, but afterwards a green uniform liquid was obtained. Meanwhile the portion of acid in the second bulb had deepened in tint, then the red oil was formed, and the other phenomena in due succession. (The weight of the acid at this point had increased). When about 4 litres of nitric oxide had passed in the green liquid in the first bulb gradually turned to a blue, which slowly evaporated into the second bulb, and eventually only a few drops of an almost colourless liquid were left. Simultaneously the portion of acid in the third bulb showed the transition tints of yellow to orange with ultimate formation of the red oil, and also dense red fumes passed out of the acid. At this point the experiment was stopped, and the weight of the nitric acid was found to have considerably decreased.

The explanation of these changes, which were observed in part by Priestley* at the end of the last century, seems to be as follows:—At first nitrogen peroxide is formed by the mutual oxidation of the nitric oxide and reduction of the nitric acid, and this is retained in solution by the excess of the acid, $2\text{HNO}_3 + 2\text{NO} = 3\text{N}_2\text{O}_4 + 2\text{H}_2\text{O}$. A point is reached at which the acid becomes super-saturated, and the excess of the peroxide separates out (the red oil). According to the experiments of Péligré, nitric oxide passed into this gives a green liquid. The absorption and retention of the nitrogen peroxide accounts for the gain in weight (about one-sixth) of the acid. The reduction then proceeds further, and nitrous acid (the blue liquid) is produced, thus: $\text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O} = 4\text{HNO}_2$, and this is evaporated by the continued current of the nitric oxide, leaving finally only the water originally present, both free and combined, in the nitric acid. This destruction of the nitric acid accounts for the loss in weight. As Priestley wrote: "Towards the end of the process (of absorption of nitrous air by pale-yellow spirit of nitre), the evaporation of the acid was perceived to be very great, and when I took it out the quantity was found to be diminished by one-half. Also, it had become by means of the process and evaporation together, exceedingly weak, and was rather blue than green."

Reaction between Nitric Oxide and Mercuric Nitrate in Nitric Acid Solution.

In my former paper (*Phil. Trans.*, 1891, A, p. 315), it was shown that when a current of hydrogen was passed through a solution of mercuric nitrate in nitric acid solution the mercuric was reduced to a mercurous salt without any considerable formation of nitrous acid, which was, however, produced in abundance when cupric nitrate was subjected to the same action. As it seemed probable that the nitrous acid which might have been produced in the former operation was in reality used up in the reduction of the mercuric salt, the experiment was repeated in precisely similar manner, nitric oxide being substituted for hydrogen. It was found, as before, that the mercuric salt was reduced; from 0.5 grm. mercuric oxide dissolved in nitric acid (1 c.c. containing 0.2549 grm. acid) after passage of nitric oxide for $3\frac{1}{2}$ hours at a temperature of 35° , 0.019 grm. of mercurous chloride was obtained, while from a similar portion, through which the nitric oxide had not been passed, 0.0018 grm. was precipitated. It is probable, then, that the hydrogen in the former experiments reduced at first the free nitric into nitrous acid, which in its turn reduced the mercuric nitrate, thus: $2\text{Hg}(\text{NO}_3)_2 + 2\text{HNO}_2 = \text{Hg}_2(\text{NO}_3)_2 + 2\text{HNO}_3$. No free nitrous acid would therefore appear in the course of the operation.

(To be continued).

ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

(Continued from p. 179).

The Reactions of other Ferric Salts and Sulphocyanates.

IN addition to the reactions of ferric chloride with potassium sulphocyanate, those of other ferric salts with other sulphocyanates were also studied. The object was to determine what change of colour effect was produced by varying the ferric salt on the one hand and the sulphocyanate on the other, and thus to obtain an insight as to the reactions taking place in the solutions. The ferric salts examined besides the chloride were the nitrate, sulphate, tartrate, acetate, and citrate. A solution of ferric nitrate was prepared by evaporating down to dryness on the water-bath a solution of ferric oxide in nitric acid. The percentage of ferric oxide in the salt was determined by ignition. It was found to contain 5.55 per cent more Fe_2O_3 than is required by the formula $\text{Fe}_2(\text{NO}_3)_6$, so the amount of standard nitric acid required to bring it to the correct percentage was added to its solution. Solutions of the tartrate, citrate, and acetate of iron were prepared by decomposing ferric sulphate with the theoretical quantities of the corresponding barium salts. By this means solutions were obtained containing scarcely any of the free acids, whilst if the solutions are evaporated to dryness and the salts so obtained dissolved up again, ferric oxide is deposited, and solutions containing considerable quantities of free acids are obtained. Besides the reactions of potassium sulphocyanate, those of the sulphocyanates of ammonium, sodium, lithium, calcium, and barium were examined. The potassium and ammonium salts used were obtained from the manufacturer in as pure a state as possible, but they were not further purified. The sodium, calcium, and barium salts were prepared by boiling aqueous solutions of the hydrates of these metals with the theoretical quantities of ammonium sulphocyanate, whereby all the ammonia was driven off. The solutions were then evaporated down and crystallised. The lithium salt was prepared by decomposing lithium sulphate with barium sulphocyanate. The calcium and lithium salts did not crystallise well, but after evaporating down the solutions to dryness on the water-bath, both set on cooling to white semi-solid masses.

The colour effects produced by mixing solutions of the various ferric salts named with those of the sulphocyanates were then determined. Two series of determinations were made: one with solutions containing a hundred equivalents of ferric salt to one equivalent of sulphocyanate; these were examined at dilutions of 160, 320, and 800 litres; the other, with solutions containing one equivalent of ferric salt to one equivalent of sulphocyanate, being examined at dilutions of 40, 80, and 160 litres. No determinations of solutions containing 100 equivalents of sulphocyanate were made for several reasons. In the first place, the previous experiments with ferric chloride and potassium sulphocyanate showed that the reactions taking place in solutions containing excess of sulphocyanate are somewhat complex, and do not take place in accordance with the law of mass, and also that these solutions are not nearly so stable as regards dilution as those containing excess of ferric salt. It is probable therefore that the colour values obtained with these solutions are due to the effects of several causes, and these may vary to different extents with different sulphocyanates, so that the values obtained would not express the true amount of reaction taking place between the salts; also it was found that sulphocyanate solutions showed slight variations in colour effect on standing, and showed slightly different colour values, according as the ferric salt was added to the sulphocyanate or *vice versa*. On standing some minutes, however, these solutions showed the same colour

* "Experiments and Observations on Different Kinds of Air," vol. i., p. 383. I may be allowed to allude to the section of this work relating to nitrous acid, which contains a number of observations upon its properties; several of them appear to have been published as novelties many years afterwards.

Salt.	Dilution in litres.	For solutions containing to 100 parts of ferric salt 1 part of sulphocyanate of—						Mean colour- constants for ferric salts.
		Potassium.	Ammonium.	Sodium.	Lithium.	Calcium.	Barium.	
Ferric chloride ..	160	9'5 × 17'2	10'0 × 15'9	10'0 × 14'6	10'0 × 10'0	11'0 × 12'2	10'0 × 12'7	10'08
" "	320	9'5 × 16'7	10'0 × 15'4	10'0 × 13'8	10'0 × 9'4	11'0 × 11'1	10'0 × 11'8	10'08
" "	800	10'0 × 14'4	10'0 × 13'0	10'0 × 12'0	10'0 × 7'5	11'0 × 10'6	10'0 × 10'2	10'17
" nitrate ..	160	10'5	9'7	10'0	10'5	10'4	10'4	10'25
" "	320	10'5	9'8	10'2	10'7	11'4	10'6	10'53
" "	800	11'3	10'0	10'2	10'9	10'6	10'6	10'60
" sulphate..	160	6'97	6'55	6'90	6'31	6'68	—	6'67
" "	320	6'36	6'20	6'77	6'22	6'82	—	6'47
" "	800	6'17	5'52	6'25	5'74	5'19	—	5'73
" tartrate ..	160	4'89	4'20	4'25	3'67	3'93	—	4'18
" "	320	3'99	3'45	3'80	3'16	3'18	—	3'52
" "	800	2'89	2'36	2'55	2'65	2'26	—	2'54
" acetate ..	160	2'05	1'82	2'01	2'00	1'64	—	1'90
" "	320	2'02	1'24	1'90	1'94	1'50	—	1'72
" "	800	1'98	1'25	1'08	1'74	1'05	—	1'42
For solutions containing to 1 part of ferric salt 1 part of sulphocyanate.								
" chloride ..	40	9'0 × 7'02	11'0 × 5'72	11'0 × 5'25	10'0 × 2'92	10'6 × 4'88	9'0 × 4'51	9'93
" "	80	9'0 × 4'08	10'0 × 3'52	10'0 × 2'78	10'0 × 1'31	10'6 × 2'43	9'0 × 1'90	9'77
" "	160	10'0 × 1'86	10'0 × 1'23	10'0 × 1'01	10'0 × 0'81	10'6 × 0'98	9'0 × 0'82	9'77
" nitrate ..	40	10'4	11'8	11'7	11'3	11'3	11'4	11'31
" "	80	11'0	11'4	12'8	11'6	11'4	11'6	11'63
" "	160	10'2	11'3	12'8	10'0	10'7	11'5	11'05
" sulphate..	40	7'51	7'97	6'44	6'13	6'64	—	6'94
" "	80	7'01	5'77	5'46	6'86	6'60	—	6'34
" "	160	6'24	7'32	8'02	7'78	6'95	—	7'26
" tartrate ..	40	2'78	2'52	2'63	2'60	2'34	—	2'57
" "	80	2'35	2'21	2'84	3'0	2'72	—	2'62
" citrate ..	40	2'35	2'08	2'17	2'23	1'84	—	2'13
" "	80	2'08	2'02	2'41	2'90	2'26	—	2'33
" acetate ..	40	1'74	1'59	1'75	2'55	1'74	—	1'87
" "	80	2'01	2'00	2'34	3'05	2'68	—	2'42

effect. With solutions containing excess of ferric salt, this was not the case. Solutions containing seven or more equivalents of ammonium sulphocyanate, when originally made up, gave colour values not far below those of the corresponding potassium sulphocyanate solutions, but on standing about half an hour or more they became quite colourless. It is probable that the ferric sulphocyanate dissolves in the excess of ammonium sulphocyanate, forming a kind of double salt; whatever it may be due to, it serves to emphasize the untrustworthiness of results obtained for solutions containing excess of sulphocyanate.

In the table are given the results obtained. The numbers are in this case compared with a different standard from those obtained in the former series, the colour effect of a solution containing to one equivalent of lithium sulphocyanate 100 equivalents of ferric chloride at a dilution of 160 litres being taken as 100, and the other values compared with this. In order to examine whether the colour values are the products of two numbers—one depending on the nature of the ferric salt, and the other on the nature of the sulphocyanate—arbitrary numbers are taken as the values due to each of the sulphocyanates at each dilution, and these are divided into the colour values obtained with the different ferric salts. It will be seen that the colour constants due to ferric chloride with the different sulphocyanates are taken as about the value 10 at all dilutions, whilst the colour constants due to the sulphocyanates are considered to vary with the dilution. Thus with ferric chloride and sodium sulphocyanate, for instance, in the 100 equivalent solutions, the numbers 14'6, 13'8, and 12'0 are taken as the colour constants due to the sodium sulphocyanate at dilutions of 160, 320, and 800 litres respectively, and these numbers are divided into the colour values obtained with sodium sulphocyanate and the other ferric salts. Each ferric salt should have the same constant colour equivalent, irrespective of the sulphocyanate it is reacting with. From the table it will be seen that such is the case, allowing for experimental error, which in colorimetric work must necessarily be

large. With ferric chloride the extreme values vary from 9'5 to 11'0; with ferric nitrate, from 9'7 to 11'4; with ferric sulphate, from 5'19 to 6'97; with ferric tartrate, from 4'89 to 2'26; with ferric acetate, from 2'05 to 1'05. It must be remembered that these variations are in great part due merely to the fact that all ferric sulphocyanate solutions are not equally affected by dilution. Thus it is evident from the last column of the table, which gives the means of the colour constants of the different ferric salts at each dilution, that whilst ferric chloride and ferric nitrate solutions are affected about equally by dilution, those of ferric acetate are affected more, whilst those of ferric sulphate and ferric tartrate are affected to a still greater extent. The different behaviour is easily accounted for when it is remembered that hydrochloric and nitric acids are monobasic acids, whilst sulphuric and tartaric acids are dibasic. With ferric sulphate and tartrate solutions a decrease of colour would occur owing to the greater formation of the acid salts in the more dilute solutions. Ostwald has shown by electro-chemical methods ("Lehrbuch," ii., 831) that the relative affinities of monobasic to dibasic acids vary according to the dilution. It will be shown later that the great decrease of the colour constants of ferric tartrate on dilution are only partly due to this cause. If the colour equivalents at a dilution of 160 litres only be taken, the extreme values for ferric nitrate vary from 10'5 to 9'7; for ferric sulphate, from 6'97 to 6'31; for ferric tartrate, from 4'89 to 3'67; for ferric acetate, from 2'05 to 1'64.

In these reactions the colour of the ferric salt was in all cases but that of the acetate so slight compared with that of the ferric sulphocyanate formed that it was not allowed for. With ferric acetate the colour is so deep and the amount of ferric sulphocyanate formed in solution so small that if one hundred equivalents are taken, almost two-thirds of the colour effect of the solution is due to this cause alone. The accuracy of the determination of the ferric sulphocyanate formed would thus be considerably impaired, so only 50 equivalents of the acetate were taken. About half the colour effect of the solution was

then due to this cause. This was of course determined and allowed for. The experiments with ferric chloride and potassium sulphocyanate show that in concentrated solutions the colour values of solutions containing only thirty equivalents of ferric salt are only very slightly smaller than for one hundred equivalent solutions, so the colour constants for ferric acetate solutions at dilutions of 160 litres and 320 litres can only be very slightly decreased from this cause. At a dilution of 800 litres they must be appreciably smaller.

(To be continued.)

ACTION OF SULPHUR IN PRESENCE OF WATER UPON THE SALTS FORMED BY THE POLYBASIC ACIDS.*

By J. B. SENDERENS.

(Concluded from p. 183).

(a) *Arsenates*.—The action of sulphur in presence of water upon the ortho-arsenates presents great analogies to that which it exerts upon the phosphates. Still, there is this distinction, that whilst phosphoric acid remains unaltered during all the reactions, arsenic acid is sometimes decomposed. Thus with the trisodium and disodium arsenates we obtain sulpharsenates and oxysulpharsenates, the formation of which is easily explained. In fact, sulphur yields at first with these two arsenates, as with the corresponding phosphates, a thio-sulphate and a polysulphide which, on decomposition, yields hydrogen sulphide. This latter gas acts upon the undecomposed arsenates so as to produce sulpharsenates and oxysulpharsenates.

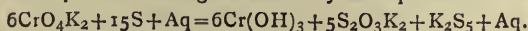
If we take this peculiarity into account, the analogy between the arsenates and the sulphates may be traced throughout. Thus the action of the sulphur ceases at the sesquibasic compound for the alkaline arsenates, but for those of the alkaline earths continues to the bibasic salt. Silver and copper arsenates are totally decomposed by sulphur, whilst the lead and nickel arsenates absolutely resist its action.

(β) *Alkaline Arsenates*.—Sulphur decomposes with boiling solutions of neutral and acid sodium arsenite. It acts at first upon the soda, forming a polysulphide, which is then decomposed with a liberation of hydrogen sulphide. This latter substance forms, with arsenious acid, arsenic trisulphide, which remains in the hot liquid, and is deposited on cooling. Sodium sulpharsenate is formed at the same time. These reactions are limited by an inverse action, that of the transformation of arsenic sulphide in contact with boiling water into arsenious acid and hydrogen sulphide, which explains the development of sulphuretted hydrogen all the time of the experiment.

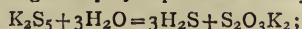
(γ) *Alkaline Chromates*.—The action of sulphur upon solutions of these salts was explained in a former communication.

With neutral potassium chromate there is produced an alkaline polysulphide which is decomposed with the formation of sulphuretted hydrogen. The reaction is determined by the free potassa of the dissolved chromate, which yields with sulphur a polysulphide and thiosulphate.

The chromic acid, on its part, is attacked by the sulphur, with the formation of chromium hydroxide. This first experimental stage is shown by the equation—

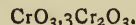


In a second stage the polysulphide is destroyed.



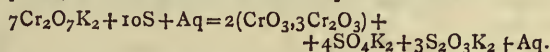
when the development of sulphuretted hydrogen commences.

With potassium bichromate we do not detect the slightest liberation of H_2S , and at no moment of the experiment does the solution contain a sulphide. This consequently excludes the action of sulphur upon the potassa of the bichromate, and establishes the strong acid function of chromic acid in potassium bichromate. According to Sabatier, chromic acid must have two functions: one of a strong acid, which appears in the formation of the bichromate; the other of a weak acid, as regards the mol. of alkali which transforms the bichromate into neutral chromate. The solutions of the neutral salt, according to Sabatier, contain neutral chromate, bichromate, and free alkali. These conclusions are confirmed by the action of sulphur upon the solutions of neutral chromate and of potassium bichromate. With the latter salt, there is formed a maroon-coloured precipitate of the composition—



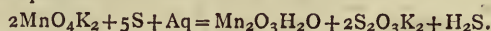
This is a chromium chromate which has not yet been described.

The liquid contains potassium sulphate, and thiosulphate, and the reaction is shown by the formula—



(δ) *Alkaline Manganates*.—The action of sulphur upon the solution of these salts presents the same peculiarities as with the chromates.

Potassium permanganate is decomposed according to the equation—



Potassium permanganate is reduced by sulphur at the ordinary temperature, yielding a hydrated manganese peroxide and potassium sulphate.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 182).

Determination of Chromic Oxide.

THE above method of determining chromic acid may also be used for an accurate determination of chromic oxide, since it is not difficult to convert chromic oxide into chromic acid. For the oxidation of the salts of chromic oxide it is preferable to use hydrogen peroxide in an alkaline solution. After the oxidation is completed, the excess of hydrogen peroxide is completely destroyed by boiling the alkaline liquid, and after neutralisation with sulphuric acid the chromic acid is destroyed by gas-volumetry.

In the analysis of chrome-iron ore, the mineral must not be opened up by fusion with soda and nitre, since large quantities of nitric acid interfere with the accurate determination of chromic acid.

We may, instead, use with advantage the process of L. P. Kinnicutt and G. W. Patterson, in which the mineral is ignited with sodium carbonate and barium peroxide, and then decomposed, not with hydrochloric acid, but with sulphuric acid.

3. *Determination of Sulphuric Acid*.—According to L. W. Andrews and H. Quantin, sulphuric acid may be effected by determining a quantity of chromic acid equivalent to the sulphuric acid. This indirect determination can, according to Baumann, be very easily executed in a gas-volumetric manner. Here, also, a solution of barium chromate comes in use.

The liquid in question, which must not contain too large an excess of hydrochloric acid, and only very small quantities of nitric acid and nitrates, is placed in a

* Bulletin de la Soc. Chimique.

* Zeit. für Angew. Chemie und Zeit. für Analytische Chemie

measuring flask holding 100 c.c. and precipitated in the cold with a solution of barium chromate in hydrochloric acid. The liquid is shaken up, allowed to stand for a short time (about thirty minutes), diluted with water to about 90 c.c., mixed with ammonia until the reaction is alkaline, filled up to the mark, and, after shaking, filtered through a dry double-folded filter. From 25 to 60 c.c. of the filtrate (according to the quantity of the chromic acid) are poured into the gas-generating vessel of the azotometer, 10 c.c. of sulphuric acid are added, and the chromic acid is determined with hydrogen peroxide in the manner already described. One c.c. oxygen at 0° and 760 m.m. barometric pressure corresponds to 1.787636 m.grms. SO_3 , or 1 m.grm. oxygen corresponds to 1.2509 m.grms. SO_3 .

In liquids containing salts of copper, so much ammonia must be added for neutralisation that the precipitate of copper formed at first is re-dissolved; instead of 10 c.c. sulphuric acid, 20 c.c. are then used for the determination.

The barium chromate to be employed must before use be repeatedly boiled up with water and then washed until the last washings no longer give a precipitate with barium chloride.

As the method yields excellent results, especially in the case of very small quantities of sulphuric acid, it may be particularly suitable for the determination of this acid in water, and principally in drinking-water; but in ash, and in substances which contain much phosphoric acid, the determination cannot be undertaken directly in the hydrochloric solution, since on neutralising with barium chromate, barium phosphate is simultaneously deposited.

The phosphoric acid must therefore be eliminated before the determination. In ashes this is effected by extraction with boiling water. The watery solution is then used at once, and the hydrochloric acid is simply neutralised. If the phosphoric acid is present in the form of an alkaline salt, it is precipitated by means of magnesia mixture. This precaution is necessary only if a considerable quantity of phosphoric acid is present. Very small quantities do not affect the accuracy of the analysis.

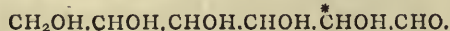
(To be continued).

THE SYNTHESIS OF SUGARS.*

By W. E. STONE, Purdue University.

(Concluded from p. 180).

It now remained to establish a connection between the synthetic sugars and the most common of the natural sugars, the grape sugar or dextrose. This is a stereoisomer of mannose (*Berichte D. Ch. G.*, xxiii., 2133); moreover their "osazons" are identical, which would show that their isomerism depends upon the asymmetry of the carbon atom indicated by the asterisk in the following formula (*Berichte D. Ch. G.*, xxii., 374) —



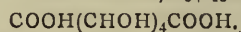
So slight a difference as this it would seem possible to overcome, although the sugars themselves are too easily decomposed to withstand such a reaction. But by heating the respective acids derived from these sugars (mannonic and gluconic) with chinolin or pyridin to 140°, it was found that the gluconic acid was converted, in part, into d. mannonic acid, and *vice versa*, the d. mannonic acid into gluconic acid. The latter was readily reduced to d. glucose, and thus the synthetic connection with the most important member of the hexatomic sugar group established. In the same way the l. mannonic acid, which it will be remembered is identical with the arabinose carbonic acid, was converted into l. gluconic acid, and this, by reduction, into l. glucose. Also, by

combining equal molecules of the d. and l. gluconic acids, there was obtained an inactive gluconic acid, which was reduced to i. glucose. The latter was also obtained by combining the d. and l. glucose, and was characterised as a syrup that fermented with yeast (*Berichte D. Ch. G.*, xxiii., 2620). It was interesting to note here that the yeast destroyed the d. glucose, or that which is ordinarily fermented in nature, rejecting the synthetic sugar precisely as in the case of the i. fructose.

This completed the series of optical isomers of the hexatomic sugar group, and showed them all to be derivatives of mannit. The list includes about twenty bodies, all produced synthetically from formaldehyd. Of these, four had been previously known as occurring in Nature, *viz.*, mannit, sorbit, glucose, and fructose. All fall into three optical classes, dextro- and lævo-rotatory and inactive. As regards their chemical constitution they include four isomeric alcohols ($\text{C}_6\text{H}_{14}\text{O}_6$),—sorbit, and d., l., and i. mannit; nine isomeric aldehyd or ketone sugars ($\text{C}_6\text{H}_{12}\text{O}_6$),—d., l., and i. fructose, d., l., and i. mannose, and d., l., and i. glucose; and six isomeric, monobasic oxy-acids ($\text{C}_6\text{H}_{12}\text{O}_7$),—d., l., and i. mannonic acids, and d., l., and i. gluconic acids. The accompanying diagram shows the synthetic relation of these to each other (see next page).

The synthesis of glucose is regarded by Fischer as the most important of all this work. He suggests that many of these synthetical products will be found in Nature. It is, however, significant that thus far only the sugars of the d. series have been found in Nature, while the first direct product of the synthesis was the inactive fructose. The course, even in a roundabout way, from formaldehyd to glucose, is regarded as important support for the theory of Von Baeyer for the formation of glucose in green plants. So also, in animal physiology, there are indicated the possibilities to be attained from the knowledge obtained concerning the structure and sources of the different sugars. For instance, the new bodies may possess nutritive values different from those of the sugars heretofore known and studied; their assimilation products may be different; and further, the sugars with more or less than six carbon atoms may produce in the animal or vegetable organism new kinds of fats and oils, or new forms of albumen. These ideas are of course speculative, but worthy of consideration.

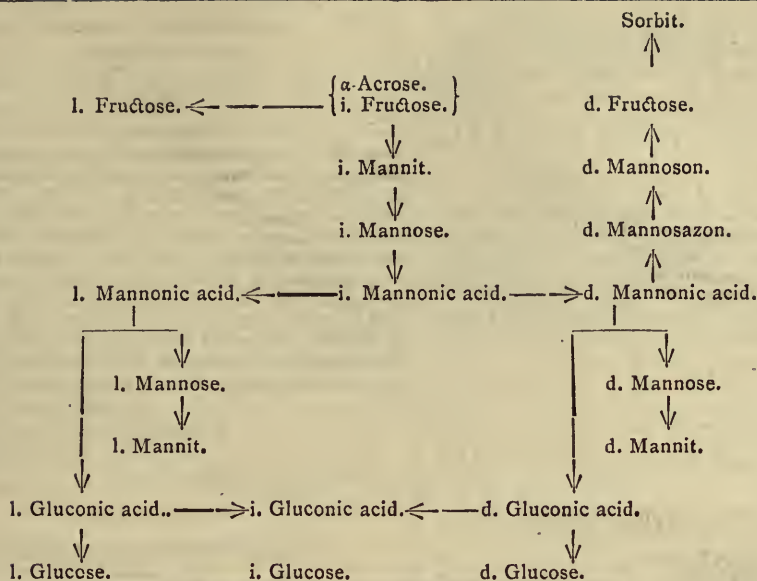
As is well known, the continued oxidation of glucose yields the dibasic saccharic acid, $\text{C}_6\text{H}_{10}\text{O}_8$, or—



Like the monobasic acids it forms a lacton which, on reduction by sodium amalgam as already described, yields an aldehyd acid, $\text{COOH}(\text{CHOH})_4\text{CHO}$, in which the carboxyl group, formerly typical of gluconic acid, has been reduced (*Berichte D. Ch. G.*, xxiii., 937). This product was found to be identical with glucuronic acid, and the synthesis of this interesting body thus established. By continued reduction the aldehyd group was reduced to an alcohol group, $\text{COOH}(\text{CHOH})_4\text{CH}_2\text{OH}$, and the new acid thus obtained was called *gulonic acid*. From this it was but a step, by means of the sodium-amalgam reduction, to a new sugar d. *gulose* which was not fermentable, or at least only with difficulty (*Berichte D. Ch. G.*, xxiv., 521). From this it appears that the *dibasic* acids derived from the sugars again offer a fruitful source for new synthetic sugars.

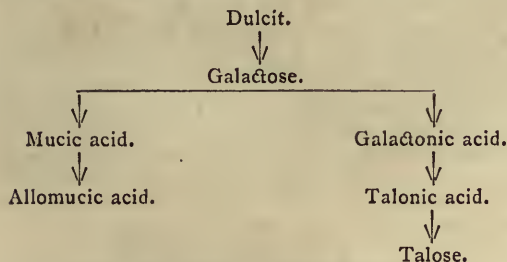
Making use of the addition of hydrocyanic acid to the aldehyds, as already described in connection with arabinose, Fischer has built up from the hexatomic sugars a series of new sugars with seven, eight, and nine carbon atoms. For instance, from d. glucose was obtained the d. glucose-carbonic acid, $\text{CH}_2\text{OH}(\text{CHOH})_5\text{COOH}$, which on reduction became gluco-heptose, $\text{C}_7\text{H}_{14}\text{O}_7$, and this in turn was built up to gluco-octose, $\text{C}_8\text{H}_{16}\text{O}_8$ (*Berichte D. Ch. G.*, xxiii., 934). Only lack of material prevented an indefinite extension of this synthesis. A similar series was obtained from d. mannose and galactose, and might

* *Agricultural Science*, vi., No. 4.



undoubtedly be had also from the l. and i. mannoses and glucoses. A noteworthy feature of the sugars thus far obtained is, that those containing three atoms of carbon or multiples of that number are fermentable, while the others are not. Glycerose, $C_3H_6O_3$, fructose, mannose, and glucose, $C_6H_{12}O_6$, and manno-nonose and glucononose, $C_9H_{18}O_9$, ferment easily.

The work thus far described had been confined to the mannit series. Of the corresponding isomeric hexatomic alcohol, dulcit, $C_6H_{14}O_6$, only one derived sugar had thus far been known, viz., galaetose. This yields, on oxidation, the monobasic galaetonic acid, $C_6H_{12}O_7$. After the successful conversion of mannonic into gluconic acid, Fischer made the same attempt with galaetonic acid by heating to 140° – 150° with chinolin or pyridin, and obtained a similar result. The galaetonic acid was transformed into an isomer, called talonic acid, which on reduction gave a corresponding sugar talose (*Berichte D. Ch. G.*, xxiv., 362). In the same way the dibasic mucic acid, $C_6H_{10}O_8$, derived from galaetose by stronger oxidation, was transformed, by heating with pyridin, into allomucic acid, the farther derivatives of which have not yet been studied (*Berichte D. Ch. G.*, xxiv., 2136). The following diagram will illustrate the achievements thus far secured in the dulcit series:—



Fischer's researches have also included the group of pentatomic sugars, which had heretofore consisted only of arabinose and xylose ($C_5H_{10}O_5$). It will be remembered that the arabinose carbonic acid was recognised as the optical antipode of d. mannonic acid, i.e., l. mannonic acid. In the same way the xylose-carbonic acid was found to be the optical antipode of the d. gulonic acid derived from gluconic acid. This l. gulonic acid gave on reduction, in the

usual way, a sugar which was the optical isomer of d. gulose, and was called l. gulose (*Berichte D. Ch. G.*, xxiv., 528). Like the d. gulose it was non-fermentable. The l. gulose was further reduced to its corresponding hexatomic alcohol, $C_6H_{14}O_6$, and this was found on careful examination to be the l. sorbit (*Berichte D. Ch. G.*, xxiv., 2144), isomeric with the d. sorbit obtained from the d. fructose.

From their ability to combine with hydrocyanic acid, arabinose and xylose are shown to be regular oxaldehyds belonging respectively to the l. mannit and l. sorbit series. Their characteristics are supposed to depend upon differences in structure, which may be expressed in the following way by the different location of the aldehyd groups:—



But in accordance with this structure they should be converted by reduction into the same pentatomic alcohol, $C_5H_{12}O_5$. Curiously enough this is not the case, the products being quite different, and it is evident that the true relation of these sugars has not yet been discovered.

Like all the aldehyd sugars, arabinose and xylose are converted by mild oxidation into monobasic acids, $C_5H_{10}O_6$. These acids, by analogy with the d. mannonic and d. gluconic acids, may be expected to undergo a transformation into their stereoisomers on heating with pyridin. Thus far this hypothesis has only been proven in the case of the arabinic acid, which yielded an isomer called ribonic acid, which was reduced to a new pentatomic sugar ribose, $C_5H_{10}O_5$. This has been but little studied, but its "osazon" melted at 154 – 155° , and it yielded a marked quantity of furfural (*Berichte D. Ch. G.*, xxiv., 4214). Studies are now in progress with the dibasic acids of the pentose sugars, which will undoubtedly result in extending the number of this group.

The discovery of so many new sugars of such close relation to each other necessitates a more systematic nomenclature than has heretofore obtained. The system proposed by Fischer classifies the sugars into groups according to the number of carbon atoms which they contain, viz., triose, tetrose, pentose, hexose, heptose, octose, nonose, &c. (*Berichte D. Ch. G.*, xliii., 2136). The proposition of Scheibler to call sugars of the formula $C_{12}H_{22}O_{11}$ "bioses," and of the formula $C_{18}H_{32}O_{16}$ "trioses" (*Berichte D. Ch. G.*, xviii., 646), is disposed of

by designating them respectively as hexobioses and hexotrioses, since they are easily decomposed to sugars of the hexose group. Again, the aldehyd or ketone sugars are specified by the terms "aldose" or "ketose." The old and well-established names dextrose and levulose lose their significance in this classification, these bodies being respectively designated by the names glucose and fructose.

The following list includes all of the known and well identified simple sugars, both natural and synthetic. Those which were known in nature or as direct derivatives of naturally occurring carbohydrates previous to Fischer's syntheses are printed in italics, by which the extent of his work is emphasised. In this list many little studied and not well characterised sugars, of occasional appearance in current literature, are not included.

Triose group, $C_3H_6O_3$:—

Glycerose.

Tetrose group, $C_4H_8O_4$:—

Erythrose.

Pentose group, $C_5H_{10}O_5$:—

Arabinose,

Xylose,

Rhamnose (methyl-pentose, $CH_3C_5H_9O_5$),

Ribose.

Hexose group, $C_6H_{12}O_6$:—

d., l., and i. glucose,

d., l. gulose,

d., l., and i. mannose,

d., l., and i. fructose,

Sorbose,

Galactose,

Talose,

Formose,

Rhamno-hexose (methyl-hexose).

Heptose group, $C_7H_{14}O_7$:—

Manno-heptose,

Gluco-heptose,

Fructo-heptose,

Gala-heptose,

Rhamno-heptose (methyl-heptose).

Octose group, $C_8H_{16}O_8$:—

Mannoctose,

Glucocose.

Nonose group, $C_9H_{18}O_9$:—

Mannonose.

Of the thirty sugars mentioned twenty are the result of Fischer's research, and to these may be added the three new alcohols, arabit, xylit, and l. sorbit, and some dozen or more of the various related acids which he has either discovered outright or has been the first to recognise in their true relations. It is not over-estimating the value of this work to characterise it as the greatest contribution yet made to the knowledge of the sugars.

Domestic Electric Lighting.—Messrs. H. Alabaster, Gatehouse, and Co. have now in the press, shortly to be issued, a new work entitled "Domestic Electric Lighting, treated from the Consumer's Standpoint." At present electricity and its varied applications are engrossing public attention to a very large extent, and the book is designed to place before intending users of electrical energy, in language as simple as possible, such matters connected with its production and distribution as will aid them to form more definite views as to their individual needs. The author is Mr. Ed. C. de Segundo, Assoc.M.Inst.C.E.

On Boyer's Method of Determining Nitrogen.—C. Arnold and Conrad Wedemeyer (*Comptes Rendus*, vol. cxiii., p. 503).—The method was designed for the determination of nitric and total nitrogen. The authors pronounce it useless, like the methods of Ruffe and of Hugo Tamm (Guyard).

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—The attention of the Council of the Institute of Chemistry has been directed to Mr. Johnstone's letter to you, which was published in the *CHEMICAL NEWS*, vol. lxvi., p. 184, and they regret to find that the leniency which was shown to him in the settlement of the action has been so greatly misconstrued by him. The statements contained in his letter are for the most part either inaccurate or misleading, but the Council are advised that, having regard to the position now taken by Mr. Johnstone, which will not improbably render further legal proceedings necessary, no useful purpose will be served by the continuance of the correspondence.—I am, &c.,

G. H. ROBERTSON,
Registrar to the Institute of Chemistry
of Great Britain and Ireland.

9, Adelphi Terrace, Strand, W.C.,
October 12, 1892.

ADVERTISING CHEMISTS.

To the Editor of the Chemical News.

SIR,—The public is constantly being advised in the advertising columns of the daily and weekly press that members of the Stock Exchange are not allowed to advertise. It is reasonable to conclude, from the absence of advertisements of licensed medical practitioners and solicitors, that the Royal Colleges of Surgeons and Physicians and the Incorporated Law Society impose some similar regulation upon their members.

Would it not benefit the chemical profession if the Institute of Chemistry were also to forbid its members to advertise themselves in the advertisement columns of the lay and technical press, and were to imitate the Stock Exchange in notifying the public of the existence of the regulation?—I am, &c.,

A. G. B.

October 7, 1892

BOGUS "FELLOWSHIPS."

To the Editor of the Chemical News.

SIR,—Some time ago there appeared in the *CHEMICAL NEWS* letters complaining of persons who fraudulently profess to be Fellows of the Royal, the Chemical, and other scientific societies, and who append to their signatures the letters F.R.S. or F.C.S., &c.

A new abuse is now springing up. Certain persons profess to be "Fellows" of societies which are not incorporated either under Royal Charter or Special Act of Parliament, and which have consequently no legal right to issue "Fellowships" at all. I would beg to caution such societies and such persons that they by no means elevate their standing by such tricks.—I am, &c.,

F.C.S.

"A NEW SILVER ORE."

To the Editor of the Chemical News.

SIR,—Your journal of July 22, which has just arrived here, contains an article on "The Recent Discovery of a New Silver Ore," by Mr. H. N. Warren. The discovery is, that the kaolin ore of the Broken Hill mines contains chloride, bromide, and iodide of silver. The presence of all these minerals in this ore was noticed by Professor Liversidge in 1886, and fully described by him at the time (*vide* "Minerals of New South Wales," pp. 39—*et seq.*).

Large specimens of the kaolin ore containing these minerals, *all named*, were in the Broken Hill exhibit at the London Crystal Palace Mining Exhibition in 1890 (*vide Mining Journal*, Aug., Sept., Oct., 1890). Your contributor also tells us that this kaolin ore containing 7 to 10 per cent of silver was for years regarded as a waste product. Here he has been misinformed. No "travelling mineralogists" were required to inform the managers of the value of this material, and if the kaolin had "remained untouched to the beginning of this year," but very small dividends would have been paid instead of the millions which have been received by the shareholders. The most absurd statement is that the ore has been tried as a material for porcelain.

The nearest manufacturing town to the mine is Adelaide, 350 miles away; porcelain is not made there, but if fire-clay were needed for that or any other purpose it could be obtained within twenty miles of the city, and a supply of even the purest fireclay would be quite worthless hundreds of miles away.—I am, &c.,

GEO. J. ROGERS.

Wallaroo Smelting Works,
South Australia, Sept. 5, 1892.

AGRICULTURAL CHEMISTRY.

To the Editor of the Chemical News.

SIR,—With reference to the review of our "Agricultural Chemistry" with which you have favoured us, and in which you are disposed to question our remarks in exaltation of farmyard manure, it occurs to us that those you have quoted apart from the context may not convey our meaning so clearly as might be, hence a few words of explanation seem desirable if you care to insert them.

Farmyard manure, as compared with many artificial manures whose value can hardly be over estimated, is of course, weight for weight, but poor stuff; its merits, however, are only properly represented when considered in connection with the part it plays in the routine of high class farming as mostly practised in this country. We have to consider the enormous quantity necessarily produced in the conversion of various crops into animal produce, and the fact of its being obtained without cost of carriage (which cripples all low class manures), except from one part of the farm to another; and especially the fact that it is the medium and diluent for highly concentrated manurial products obtained from cakes, &c., which form a material element in their value, and the importance of which we have endeavoured to illustrate in our new introductory remarks.

Again, in regard to sewage manures our poor opinion of these refers to manures obtained by precipitation from sewage, as it occurs in the sewers of London and other large towns, where the valuable constituents are diluted with an enormous proportion of water. The instances you mention of manures yielding 3 per cent of ammonia and 5 per cent phosphates could hardly refer to any products obtained on a commercial scale from this source, but probably to excrementitious materials procured without the use of water; of such material, or at least the liquid portion of it, we have spoken most favourably, and referred to it as a neglected source of manurial nitrogen.—I am, &c.,

ALFRED SIBSON.

23, St. Mary Axe, E.C.,
October 8, 1892.

SEWAGE MANURES.

To the Editor of the Chemical News.

SIR,—The sewage manure referred to in our notice of Messrs. Sibson's work on "Agricultural Chemistry" was obtained from water-carried town sewage without any addition of phosphates or nitrogenous matter. But no

lime had been used in their production either in precipitation or during the drying-process. The analyses have been made by competent and disinterested chemists.—I am, &c.,

YOUR REVIEWER.

STILLS AND THE EXCISE.

To the Editor of the Chemical News.

SIR,—Some few months ago I applied to H.M. Commissioners of Inland Revenue, asking for a license to enable me to purchase the old form of methylated spirit (*i.e.*, free from naphtha). My application had the effect of causing my laboratory to be visited by no less than four Government officials, who, during their inspection, discovered that I used stills and retorts for various analytical purposes. I was told that I had no right to use any form of still or retort without paying a license of ten shillings and sixpence, and I was duly served with a notice that I must take out such a license before a certain date. Even Hogg's Patent Still, in which the water is merely condensed against a cold inverted cone, from the apex of which the condensed water drops into a cup and is conveyed outside the apparatus, was considered to be a "still" within the meaning of the Act. Having made enquiries, and finding that very few, if any, chemists paid such a license, I refused to pay, and after a correspondence extending over several months, I have at last obtained, chiefly, I believe, through the efforts of Mr. G. H. Robertson, the secretary of the Institute of Chemistry, the necessary permission to use stills and retorts "for the purposes of my profession." My excuse for troubling you with this letter is, that I believe few analytical chemists are aware that it is necessary to obtain the permission of the Inland Revenue Authorities in order to use ordinary glass retorts and stills.—I am, &c.,

P. GERALD SANFORD, F.I.C.

Laboratory, 20, Cullum St.,
London, E.C.

Determination of Tartar in Sweet Wines, according to the Method of Berthelot and Fleurién.—Dr. E. Ackermann.—In a treatise entitled "Does Every Wine contain Tartar?" Petrowitsch, of Zombor, gave the following figures as the composition of a pure Karlo-witz wine:—

Specific gravity	1.0421
Alcohol (by volume)	14.65
Total acid, calculated as tartaric acid. ..	0.82
Extract	12.65
Sugar	6.76

In the determination of tartar, according to the method of Berthelot and Fleurién, not the smallest trace of tartar was deposited after standing for some days, and he therefore concluded that none was present. There was instead deposited at the bottom of the flask a tough, slimy, brown substance, which the writer considered to be chiefly colouring-matter. Hence Petrowitsch concluded that no tartar was present, but that it had all been precipitated by the alcohol whilst kept in a very cold cellar. Dr. Ackermann obtained a similar deposit from a sweet Greek wine, and found that it consisted chiefly of sugar mixed with tartar. The wine contained 0.8 grm. tartar per litre. Tartar is therefore not necessarily absent in wines containing 14.8 per cent by volume of alcohol. In sweet wines the sugar prevents the crystalline deposition of tartar partially or entirely, according to its quantity. The method of Berthelot and Fleurién is therefore not applicable to sweet wines unless before precipitation they have been thoroughly fermented with a mixture of ether and alcohol.—*Zeit. für Analytische Chemie*, Vol. xxxi., Part 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 13, September 26, 1892.

Suberene, a New Hydrocarbon.—W. Markownikoff.—This compound, on reacting with aluminium bromide, forms a compound, $C_6Br_5CH_3$. Its melting-point is 283° .

Action of Piperidine and Pyridine on the Haloid Salts of Cadmium.—Raoult Varet.—The author has formed and examined the piperidine chlorocadmiate, the A and B bromocadmates, and the A and B iodocadmates; as also the pyridine chlorocadmiate, bromocadmiate, and iodocadmiate.

Zeitschrift für Anorganische Chemie.
Vol. xxx., Part 6.

Reaction of Ferric Salts with Soluble Sulphocyanides.—Gerhard Krüss and Hermann Moraht.—Some time ago the authors sought to utilise the spectro-photometric method proposed by K. v. Vierordt for the determination of small quantities of iron, and carry out such determinations, using Vierordt's constant A for the light-absorbing power of iron sulphocyanide. An extended series of experiments showed them that this method led to incorrect results, since the light-obscuring powers of two solutions of iron sulphocyanide for any spectral region is not proportional to the concentration of these solutions. Not merely acids and saline solutions but even water, according to the author's experiments, occasions a dissociation of the red iron compound. A year ago Magnanini (*Rendiconti della R. Accademia dei Lincei*) studied the same iron reaction by means of quantitative spectral analysis, and obtained results which confirm the dissociability of the coloured iron sulphocyanide by water and thus testify against the possibility of a spectrophotometric determination of iron. J. Riban also made a critical repetition of our measurements of the spectrum of iron sulphocyanide and arrived at the same results. As to the analytical phase of the reaction between ferric salts and soluble sulphocyanides, the results of Riban and of the authors seem to contradict the recent observations of M. Lapicque. But this contradiction turns on an insufficient distinction between colorimetry and spectro-colorimetry. In a colorimetric manner small quantities of iron may certainly be determined. Thus Mylius and Foerster made use of the sulphocyanide reaction for determining small quantities of iron. It is needful to keep the solutions to be compared in the same stage of dissociation by the addition of equal quantities of sulphocyanide, hydrochloric acid, and water. The authors then proceed to a theoretical explanation of the course of the reaction of soluble sulphocyanides upon ferric salts.

New Process for the Formation of Basic Copper Sulphates.—L. Marchlewski and J. Sachs. If a saturated watery solution of copper sulphate is heated on the water-bath with an excess of the bases dimethylaniline, diethylaniline, and quinoline, the salts formed by the intervention of the two former bases are identical, and correspond to the formula $6CuO, 2SO_3, 5H_2O$, whilst the salt formed in presence of quinoline is $8CuO, 3SO_3, 10H_2O$.

The Quantitative Separation and Determination of Chlorine, Bromine, and Iodine.—Carl Friedheim and R. Jos. Meyer.—The substance of this paper will be given at some length.

A Contribution to a Knowledge of the Complex Inorganic Acids.—F. Kehrmann.—A communication from the Inorganic Laboratory of the Technical High

School at Aix la Chapelle. The author examines the phosphotungstic acid with 24 atoms of tungsten, that with 18 atoms, that with 22, those with 21 and with 7, and notices several series of salts which he has obtained but not thoroughly examined. He summarises his investigations as follows. On bringing together tungstates with phosphoric acid or phosphates under different experimental conditions, there ensues the formation of a considerable number of complex salts containing tungstic acid, phosphoric acid, and a base, and being generally hydrated, the acid may in many cases be obtained free, whilst in other salts it is permanent only in combination. If the series of salts thus obtained are subjected under various conditions to the action of acid or alkaline reagents there arise new series of salts by the fissions of the molecules, which again may be further split up by the same means. The number of the compounds already thus obtained or obtainable is very large. But in spite of the great difficulties which the analyses present, the constitution of these puzzling complex acids is possible only by means of a penetrative qualitative and quantitative study of the processes of scission.

Trihaloid Compounds of Rubidium and Potassium.—H. L. Wells and H. L. Wheeler.—The authors have been led to place the trihalogenides in the class of the so-called double halogen compounds. All the potassium compounds can be obtained with identical halogen atoms, whilst in the missing rubidium halogenides the halogen atoms are different.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Monazite.—Messrs. Richard Baker, Son, and Co. will find a description of this mineral and the places where it is found in the "Manual of Mineralogy and Lithology," by Mr. James D. Dana, of New Haven, Connecticut. Messrs. Trübner and Co., of Paternoster House, Charing Cross Road, London, are the publishers of the work. —WILLIAM BROWN.

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THE CHEMICAL NEWS.

Vol. LXVI., No. 1717.

NOTE ON THE ACTION OF DRY SULPHUR DIOXIDE ON OXY-SALTS.*

By DR. W. R. HODGKINSON, F.R.S.E.,
and J. YOUNG, A.R.S.M.

THE behaviour of sulphur dioxide on solutions of certain oxy-salts, such as nitrates and chlorates, is sufficiently well known, and in fact a matter of everyday occurrence. The reactions of the dry gas on these salts does not, however, appear to have been carefully studied.

Some quantitative experiments have therefore been made with several typical salts. The mode of experiment has been to expose a weighed quantity of the salt to a current of carefully dried SO_2 in a tube so arranged that it could, if necessary, be heated to some definite temperature in an air-bath, or with the naked flame if desired.

Nitrates.—A considerable number of nitrates have been examined. As a rule the action commences at the ordinary temperature, coloured oxides of nitrogen are given off, and when the salt is employed in fine powder the temperature rapidly rises, and the metal in every case is completely converted into sulphate. As long as the materials were quite dry no SO_3 was formed beyond that necessary to form sulphate with the metal. Silver nitrate taken, 1.7068 grm.; sulphate found, 1.5660 grm.; calculated, 1.566 grm. Potassium nitrate taken, 0.9490 grm.; sulphate found, 0.816 grm.; calculated, 0.817 grm.

Chlorates.—The only salts of this class examined were those of barium and potassium. The first result of impact of the SO_2 was the liberation of chlorine peroxide, which escaped along with the excess of SO_2 as long as the temperature did not rise above 60° . At a little higher temperature there was a slight flash in the tube, and formation of white fumes of SO_3 . The escaping gases then contained chlorine, SO_3 , and SO_2 . The yellow but clear mixture of sulphur dioxide and chlorine peroxide became cloudy from formation of SO_3 on introduction of a little moisture. Moist SO_2 appeared to act more rapidly than dry, and in most cases without visible liberation of chlorine peroxide. Barium chloride taken, 0.480 grm.; found as sulphate, 0.364 grm.; calculated, 0.367 grm. Potassium chlorate taken, 1.0082 grm.; found as sulphate, 0.7798 grm.; calculated, 0.7797 grm. Phosphates are apparently not acted upon at all by SO_2 .

With chromates, dichromates, and permanganates considerable differences of behaviour were noticed, depending evidently on the nature of the metal. With silver chromate the figures point to the formation of silver sulphate and chromic oxide. Silver chromate taken, 0.9348 grm.; after heating to near redness weight found was 1.0934 grm.; for a mixture of sulphate with chromic oxide it should be 1.092.

With alkaline chromates, dichromates, or barium chromates there is an evident tendency to form chromium sulphate as well as other sulphate. In no case, however, has the formation of chromium sulphate proceeded its full extent, even when the heating has been continued for many hours in a steady current of SO_2 . Permanganates behave in a similar manner.

With both classes of salts the action is at first rapid during the formation of the more positive sulphate, and ceases at a higher temperature owing to the decomposition of the chromium and manganese sulphates by heat.

	Grms
Potassium bichromate taken	1.6214
After heating in SO_2	2.0256
After re-heating for two hours in SO_2	2.0468
Calculated as a mixture of Cr_2O_3 and K_2SO_4 it would be	1.7945
As a mixture of K_2SO_4 and $\text{Cr}_2(\text{SO}_4)_3$	3.1214
Potassium chromate taken	0.907
After heating for half an hour in SO_2	1.1675
After re-heating for two hours in SO_2	1.2606
Calculated as a mixture of K_2SO_4 and Cr_2O_3	1.1688

The ease with which potassium nitrate was converted into sulphate by the action of dry SO_2 suggested a method for the determination of potassium in gunpowder and similar substances. It was, however, found very unsuitable.

A number of experiments carried out by Lieutenant L. E. Traherne, R.N., show that when gunpowder is acted upon by SO_2 at about 150° , either dry or moist, the temperature rises rapidly, and causes in most cases explosion. With fine-grained powders, and especially when unglazed, the action is more rapid and the explosion violent, as it appears to take place over a considerable area at once.

Chlorates, as might be expected, when simultaneously in contact with SO_2 and any kind of organic matter, set up a violent action. A good form of lecture experiment is to allow one or two drops of a solution of SO_2 in alcohol or ether to fall on a little powdered potassium chlorate; white fumes are given off, which are nearly always followed by a sharp explosion.

ACTION OF AN ELECTRIC CURRENT UPON THE GROWTH OF SEEDS.

By Dr. JAMES LEICESTER,
Lecturer on Chemistry at the Merchant Venturers'
Technical School, Bristol.

A SHORT note with regard to the above subject has already appeared in the CHEMICAL NEWS: further experiments have been performed with the following results:—

The current has no action, as far as can be observed, upon the growth of plants.

An improvement upon the zinc and copper plates is obtained by using a Daniell's cell; this yields a much stronger current, the current obtained from the plates being only noticeable with the aid of a mirror galvanometer.

Lettuce seeds are the best to illustrate the quicker growth. It appears that the current only acts until the initial store of food in the seed has been used up.

Whether a stronger current than we have so far used would in some way bring the plant food quicker remains to be tried.

NOTE ON THE REICHERT PROCESS FOR BUTTER AND OTHER FATS.

By J. ARTHUR WILSON.

THE Reichert process, which to-day stands in the front of any single method for the analysis of butter-fat, has since its introduction undergone very considerable change, due to the united experience of chemists in all parts of the world. The most noticeable improvements have been those of Meissl, Allen, and, lastly, of Woolny, who, in an elaborate paper (translated in the *Analyst*, xii., 201) has studied the errors and imperfections of the process, and who has formulated a method of working which, if properly carried out, gives the best possible results.

* Read before the British Association Edinburgh Meeting, 1892

Richmond (*Analyst*, xvii., No. 197) has reviewed the history of this process and its modifications, especially with regard to the limit of various observers. There is one point which seems to have occupied notice, namely, the *increased rate of distillation of volatile acids, with increase of salts in solution*. This was observed long ago by myself in the case of acetic acid, and the effects of varying proportions of salts of the alkalis, especially, determined (see the *Four. Soc. Chem. Ind.*, x., No. 1). It is therefore very necessary that in all such determinations as the Reichert or Woolny value the same quantity of alkalis and acids must be employed; otherwise, exact agreement between two operators will be impossible. If sodium hydrate be used in place of potassium hydrate, as in the Woolny process, then there will not be the agreement one might expect. The same remark applies to the substitution of oxalic acid or phosphoric acid for the sulphuric acid usually employed for liberating the fatty acids.

The exact determination of the influence of salts on the process as carried out in actual practice would be interesting and valuable.

Tottington Mills, October 3, 1892.

ON THE DETERMINATION OF WATER AND OF FREE FATTY MATTER IN SOAP.

By J. ARTHUR WILSON.

THE usual method of determining water in soap by drying a weighed quantity of the sample, cut into thin shavings, at increasing temperatures up to 110° C., does not give the most accurate results, and, besides, is frequently very tedious. Watson Smith's modification has in my hands not been successful, especially with highly watered soaps. The free fatty matter is also very frequently considerably in error when done by the old process, especially when extraction is continued for only four hours.

By the methods to be now described, the time required for both determinations is materially shortened and greater accuracy obtained.

Water Determination.

About 2.5 grms. of the sample is weighed out in a thin flat-bottomed porcelain dish, 3 inches diameter and 0.5 inch deep (such as are used for total solids in milk analysis). It is gently melted, and 5 c.c. of absolute alcohol added, and the dish warmed on the water-bath till soap is dissolved; whereupon about 10 grms. of ignited sand is added and incorporated with the dissolved soap: the dish is afterwards placed on the water-bath for one hour. 5 c.c. of absolute alcohol is then poured over the sand, then the dish is placed in the air-bath at 100–105° C. till constant weight is attained. With ordinary soaps, and the use of the improved air-bath, this will be in about three hours; whilst highly watered soaps require about five or six hours.

Determination of Free Fat.

The residue from the water determination is ground up in a glass mortar, and transferred to the Soxhlet tube, and exhausted with re-distilled petroleum ether; two hours being sufficient under these conditions. The Soxhlet tube should have a mercury seal and ground joints in place of corks.

Modifications.

If the sample contains free caustic alkali (easily seen by dropping a little phenolphthalein on a clean surface of the sample), the residue from the water determination cannot be used for the determination of the free fat, on account of the saponification of the latter by the free alkali. In such a case, the ordinary method of determining the

water is adopted, but it is not necessary to prolong the drying more than four hours. The dry residue is then ground up with 10 grms. of sand, transferred to the Soxhlet, and exhausted as before.

The improved process for free fat determination gives higher results for the same reason that the paper coil and plaster processes do in milk analysis.

Tottington Mills, October 6, 1892.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Continued from p. 191).

Summary of Results.

I. The reaction between nitric oxide and nitric acid varies with the concentration of the acid and the temperature; with more concentrated acids nitrogen peroxide is at first formed and then nitrous acids; with less concentrated acids the latter is produced at once.

II. Only with quite dilute acids (of 30 per cent concentration and below) does the reaction between the nitric oxide and nitric acid appear to be reversible; the average value for $p/q = 9$ (p = quantity of nitric, q of nitrous, acid), though the actual value varies from 3 to 4 per cent on either side according to the conditions of the experiment.

III. With more dilute acids the amount of nitrous acid formed increases slightly and then decreases with the temperature; but with more concentrated acids the amount uniformly decreases.

IV. The proportional quantity of nitrous acid formed increases with decrease of concentration, but the actual quantity is of course less.

It would appear that the simple reversible reaction between nitric oxide and nitric acid becomes modified with acids above a concentration of about 30 per cent and a temperature of 32°. These were also approximately the limits of concentration and temperature, above which the reactions between metals and nitric acid could not be prevented by substances such as urea, potassium chlorate, and the like. I will, however, merely allude to the point without wishing to lay an undue stress upon possibly nothing but chance coincidences.

The Rate of Decomposition of Nitrous Acid.

The velocity of the decomposition of nitrous acid, presumably in nitric acid solution, has been made the subject of a previous investigation by Clemente Montemartini (*vide supra*). As a result of several series of experiments this writer considers that the rate of this decomposition may be expressed by the differential equation—

$$(I). \frac{dC}{dT} = kC \quad \text{or} \quad (II). k = \frac{1}{T} \log \frac{C_0}{C_1}$$

in which C is the concentration, T the time, and k is a constant.

This equation will be discussed in the sequel. My experiments were commenced primarily with a view of ascertaining if nitrous acid is the more stable the greater the proportion of nitric acid present, a point which was raised in the course of my investigations on the reactions of nitric acid and metals. Further, it seemed probable that the presence of metallic salts might also affect the stability of nitrous acid, as Armstrong and Acworth (*Chem. Soc. Journ.*, 1877, ii., p. 54) allude to the persistence with which the nitrous acid is retained by solutions containing the products of the reaction between nitric acid and metals. It also seemed possible that such a line of inquiry might throw some light upon the nature of an acid intermediate between nitrous and nitric acids, in

* A Paper read before the Royal Society, June 2, 1892.

whose existence certain writers believe, though the facts adduced at present are perhaps hardly sufficient to warrant such a belief.

The apparatus and method of experiment finally adopted were as follows:—The nitrous acid solution was placed in a cylindrical tube containing 100 c.c. up to a certain mark; at its upper end were two apertures, into one of which was sealed a glass delivery tube, while the other could be wholly or partially closed by a small rubber plug through which passed a pipette of exactly 2 c.c. capacity. The former, which served for the passage of a stream of carbonic acid, was sealed off at its lower end, the gas passing through a small pinhole at the side, and thus not directly impinging upon the liquid; the space between the loosely-fitting plug and the glass wall serving for its exit. At the end of certain intervals of time the plug was rammed in, whereby the pressure of the gas forced the liquid up the pipette: when this was filled up to the graduation mark the sample was removed for analysis, while the aperture of the cylindrical tube was partly closed meanwhile by a duplicate plug. The cylinder was immersed in a water-bath, the temperature of which was kept constant to within one-tenth of a degree on either side of that required. Before any observations were made the ratio of nitrous to nitric acid present was determined.

Nitrous Acid from Silver Nitrite and Hydrochloric Acid.

The solution of nitrous acid was prepared in the usual manner by the decomposition of re-crystallised silver nitrite with a slight deficiency of hydrochloric acid, and the liquid filtered from the precipitated silver chloride into the decomposition flask. The amount of nitrous acid was determined at the end of fixed intervals of time, generally half an hour, and the results calculated on the hypothesis that the volume of the liquid was maintained constant throughout the course of the experiment.

In the following Table the results obtained are set forth, in which T is the time from start and C the concentration of the solution.

SERIES XXIII.

Volume of solution = 60 c.c. Temperature, $24.9^{\circ} \pm 0.1$.
Ratio of nitrous to nitric acid = 1:3.86.

T.	C.	T.	C.
	Grm.		Grm.
0	0.3063	120	0.2306
30	0.2793	150	0.2130
60	0.2559	180	0.2017
90	0.2413	210	0.1890

These results are expressible by the formula—

$$\log(T+t) + \log C = \log k,$$

in which T is the time from start, and t an interval of time which would have elapsed from the moment at which, conditions remaining otherwise the same, the amount of nitrous acid was infinitely great, namely, $C = \infty$, and that moment at which the experiment was actually commenced, C is the concentration, and k is a constant.

In the above series the value for t is taken as 320', and in the Table below are given the values for $\log(T+t)$, $\log c$, and $\log k$.

Log (T+t).	Log C.	Log k.
2.5051	1.4861	1.9912
2.5441	1.4461	1.9902
2.5798	1.4080	1.9878
2.6128	1.3825	1.9953
2.6335	1.3629	1.9964
2.6627	1.3283	1.9910
2.6901	1.3046	1.9947
2.7160	1.2764	1.9924

lated therefrom, the observed and calculated values for the concentration of the nitrous acid will compare as follows:—

C (observed).	C (calculated).	C (observed).	C (calculated).
Grm.	Grm.	Grm.	Grm.
0.3063	0.3071	0.2306	0.2285
0.2793	0.2808	0.2130	0.2138
0.2539	0.2586	0.2017	0.2006
0.2413	0.2397	0.1890	0.1890

The greatest difference occurs in the third value, which is rather less than 2 per cent, which can readily be accounted for by errors of experiment in dealing with a substance so susceptible of decomposition as nitrous acid. The curve which represents the concentration of the acid in terms of time is a portion of a hyperbola, the differential equation of which is—

$$\frac{dC}{dT} = -\frac{C^2}{M},$$

which expresses the rate at which equivalent masses react, whether it be of the nitric with the nitrous acid, or the nitrous acid with itself; in each experiment $1/M$ is the amount of each unit mass which reacts with the other per unit time when an unit mass of each substance is present.

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be perfectly clear, bright, and well filtered, the somewhat considerable rainfall on the 21st and 22nd September, amounting at Oxford to 0.76 of an inch, being without obvious effect on the subsequent supply. There was also a fall of 0.71 of an inch on the last day of the month.

In respect to the smallness of the proportion of organic matter present, the character of the water furnished by the seven companies continued to be entirely satisfactory, the mean amount of organic carbon in the Thames-derived supply, for example, being 0.118 part, and the maximum amount in any single sample examined being but 0.145 part, in 100,000 parts of the water—numbers practically identical with those of the previous month, or

The values in the third column show great concordance; if the mean 1.992 be taken and the results calcu-

0.115 part for the mean and 1.52 part for the maximum amount.

As observed in previous reports, so long as the amount of organic matter in the water supply, as estimated alike by the combustion and oxidation processes, continues absolutely small, the seasonal variations in amount are of no practical significance. With the coming on of autumn and winter, however, it is not to be expected that the low average of the past six months will be much longer sustained; this average, in the case of the Thames-derived supply, amounting only to 0.116 part of organic carbon in 100,000 parts of the water, with a maximum, twice met with, of 0.152 part in any individual sample. It is to be noted that the water supply to London is habitually at its best during the hot season, when a high quality of the supply is more especially called for.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.

ON THE REACTIONS OF FERRIC SALTS WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

(Continued from p. 193).

IN solutions containing one hundred equivalents of ferric citrate the colour due to the ferric sulphocyanate formed was so much masked by the yellowish brown colour of the citrate that no proper measurements could be made. It was not possible to allow for the colour effect due to the citrate, as its colour was so totally different from that of ferric sulphocyanate. It was not possible in most cases to determine the colour effects of barium sulphocyanate with ferric salts, as precipitates were formed. This was the case even in the equal equivalent solutions. Also, the colour reactions of sulphocyanates with ferric oxalate could not be determined, as the large quantity of free oxalic acid, which must be present to keep in solution the ferric oxalate, decomposes almost all the ferric sulphocyanate, so that the colour effect produced is too small for accurate measurement.

With solutions containing equivalent quantities of ferric salt and sulphocyanate, the colour constants show a general similarity to the constants for the former series, but they differ from them in several respects. Thus the constants for ferric nitrate are considerably larger than those for ferric chloride, whilst in the former series they are only slightly larger. The constants for ferric sulphate are slightly greater than before, but whilst those for ferric acetate are also larger, those for the tartrate are considerably smaller. In the paper before alluded to the author showed that ferric tartrate decomposed greatly in dilute solutions, with formation of ferric oxide. It is to this that the small colour constants for ferric tartrate are due. In the 100 equivalent solution at 160 litres dilution the solution of the salt is moderately concentrated, and therefore but little of it is decomposed; but in this solution at 800 litres dilution, and in the equal equivalent solutions where it is more dilute, the colour constant is not much more than half what it should be, as the portion of the tartrate decomposed no longer reacts with it. The colour values for ferric tartrate, citrate, and acetate solutions at 160 litres dilution were so small that they could not be determined with any approach to accuracy. They are accordingly omitted from the Table.

With solutions containing 100 equivalents of ferric chloride the colour constants for the various sulphocyanates decrease to very nearly the same extent on dilution from 160 litres to 800 litres as for potassium sulphocyanate; and as the proportion of ferric sulphocyanate in these solutions decrease on dilution according to the law of

mass, the law holds with the other sulphocyanate solutions. As the colour constants for ferric nitrate do not vary on dilution, the ferric sulphocyanate in solutions of ferric nitrate and sulphocyanates is also affected by dilution in accordance with the law of mass. With ferric sulphate solutions, however, the colour decreases at a greater rate than in accordance with the law, as is shown by the decrease in the colour constants at 800 litres dilution.

An explanation has already been afforded of this, and also of the abnormally great decrease of colour of ferric tartrate solutions on dilution. The colour decrease of ferric acetate solutions is due to the same cause as that of the tartrate solutions, for ferric acetate solutions are also largely decomposed on dilution, with formation of free ferric oxide.

Solutions containing equal equivalents of ferric chloride or nitrate and the various sulphocyanates appear to obey the law of mass moderately well. Those for ferric sulphate show great irregularities, the colour constant seeming to decrease at 80 litres dilution and to increase again on further dilution. Ferric citrate and acetate solutions also show slightly greater constants at 80 litres than at 40 litres dilution. Taken as a whole, the numbers for equal equivalent solutions show much greater irregularities than those for solutions containing 100 equivalents of ferric salt, and they are evidently not nearly so trustworthy. With 100 equivalent solutions many of the errors which are very large with equal equivalent solutions dwindle down to insignificance. Thus the amount of ferric sulphocyanate formed does not vary much with dilution, and would indeed be little greater at infinite concentration, the point at which the colour values should be theoretically determined, than at 160 litres dilution. With equal equivalent solutions it has been shown that the colour value at 40 litres is only about a fourth its value at infinite concentration, and as it is not known for certain whether the amount of ferric sulphocyanate in the various solutions varies with the dilution according to the law of mass, the colour values found may be far from proportional to the true value at infinite concentration. Again, there is not so much likelihood of the formation of basic salts, and if such were formed, not nearly so much error would be introduced as with equal equivalent solutions, in which the removal of a part of the ferric salt in this way would mean the non-formation of a corresponding amount of ferric sulphocyanate.

With regard to the nature of the colour constants of the various ferric salts and sulphocyanates, it is evident that they must depend on the relative affinities of the various acids and bases reacting in the solution. Thus, in a solution of ferric chloride and potassium sulphocyanate there are also present ferric sulphocyanate and potassium chloride, and the amount of ferric sulphocyanate formed depends, on the one hand, on the relative affinities of hydrochloric acid and sulphocyanic acid for ferric oxide, and, on the other hand, on the relative affinities of these acids for potash.

In the Table are given the colour constants of the various acids the ferric salts of which were used, and of the various bases the sulphocyanates of which were used. The means of the numbers are given for 100 equivalent solutions for 160 litres dilution, and the means of the numbers for all three dilutions. The means of the numbers for all the dilutions for equal equivalent solutions are also given. The colour constants of hydrochloric acid and of potash are taken as 100, and the other values compared against these. The coefficients of affinity, as determined by electro-chemical methods (Ostwald, *Lehrbuch*, ii., 823 and 839) are given, and also those of the acids as determined by saponification of methyl acetate (Ostwald, *Lehrbuch*, ii., 803) and of the bases by saponification of ethyl acetate (R. Warder, *Amer. Chem. Journ.*, 1882).

There are considerable resemblances between the colour constants of the acids examined and the electrical conductivities. If the colour constants for 100 equivalent solutions at 160 litres dilution—which are un-

Acid or base.	Means of constants for 100 equivalent solutions at 100 litres dilution.	Means of constants for 100 equivalent solutions at all dilutions.	Means of constants for equal equivalent solutions.	Electrical conductivities.	Velocity constants as shown by saponification of methyl and ethyl acetate.
Hydrochloric	100	100	100	100	100
Nitric ..	101.7	103.5	115.4	99.6	92
Sulphuric ..	66.2	62.2	69.7	65.1	73.9
Tartaric ..	41.5	33.7	26.5	2.28	2.30
Citric ..	—	—	22.6	1.66	1.63
Acetic ..	18.8	16.6	21.8	1.424	0.345
Potash ..	100	100	100	149	2.298
Ammonia ..	92.4	91.9	80.8	4.8	0.011
Soda ..	84.9	86.1	69.7	161	2.307
Lithia ..	58.1	55.7	39.0	142	—
Lime ..	70.9	69.1	63.9	—	2.285
Baryta ..	73.8	71.9	55.8	—	2.144

doubtedly the most trustworthy—be compared with the electrical conductivities, the values for sulphuric acid, compared with those for hydrochloric acid, differ by less than a unit. The conductivity of nitric acid is slightly smaller than that of hydrochloric acid, whilst with the colour constants the reverse is the case. The difference is, however, within the limits of experimental error, as even the electrical conductivity values are liable to an error of two or three per cent or more. Though the colour constants of tartaric, citric, and acetic acids are considerably smaller than those of the other acids; and though they are of the same order as the electrical conductivities, that of tartaric acid being most, and of acetic acid least, yet they bear no numerical resemblance to them. The value for tartaric acid is eighteen times as large as the conductivity, and that of acetic acid thirteen times as large. The colour constant for citric acid could not be determined for 100 equivalent solutions, but the constants for equal equivalent solutions show that it lies between the numbers for tartaric acid and acetic acid, as its conductivity does.

It is thus evident that there is a considerable general resemblance between the colour constants and the conductivities of the acids examined, even if there is not a numerical one. The colour constants for the bases show scarcely any resemblance to the conductivities. Thus soda has a greater conductivity than potash; its colour constant is considerably less. The conductivity of ammonia is not a thirtieth that of soda; its colour constant lies between those of potash and soda. The colour constant of lithia is considerably smaller than those of soda and potash; but its conductivity, though smaller than those of soda and potash, does not differ from them much. The colour constants for lime and baryta are nearly equal, and are slightly smaller than the value for soda. This is the sole resemblance between these numbers and the affinity coefficients; for the velocity constants of lime and baryta are also similar, and slightly smaller than the value for soda. Why the colour constants for the bases should exhibit such slight resemblance to the conductivities, when for the acids there is considerable similarity, it is not possible to say. If determinations of the colour constants of solutions containing 100 equivalents of sulphocyanate could have been properly carried out, a greater resemblance might perhaps have been found to exist.

Whatever resemblance or otherwise the colour constants of the acids and bases examined bear to their affinity coefficients, it is nevertheless evident that the amount of ferric sulphocyanate formed in a solution containing a ferric salt and a sulphocyanate is proportional to the product of two numbers, one depending on the nature of the acid and the other on the nature of the base. It is not in any way possible to express the amount of ferric sulphocyanate produced in the form of a sum of

two quantities. This rule, found to obey for ferric salts and sulphocyanates, must hold for all salt solutions, so that when any two salts are mixed in a solution it follows that, no precipitate being formed or no product being otherwise removed from the solution, the quantities of the fresh salts formed by their interaction are proportional to the product of two constants. The quantities of the original salt still remaining of course depend on a similar rule. The final proportions of the salts formed depend on a balance between these two contrary reactions. The salts are probably formed according to the same rule, whether they are partially or wholly dissociated in solution or not.

(To be continued).

THE USE OF FLUORIDES IN THE MANUFACTURE OF ALCOHOL.*

By Dr. LEO BAEKELAND.

DR. EFFRONT'S researches on the antiseptic properties of fluoride compounds have lately received important applications in the alcohol industry, and a condensed statement upon this subject may be of interest not only to alcohol manufacturers, but also to the biological chemist.

It is a known fact that for the transformation of starch into maltose and dextrin by the action of diastase, the most favourable temperature is from 50 to 60° C. At any lower temperature the action of the diastase becomes slower, while a higher temperature has a destructive effect upon this soluble ferment, which at 80° C. completely loses its saccharifying power.

In laboratory experiments where pure starch and pure diastase can be used it is possible to exclude all secondary influences from other ferments. In practice, however, conditions are far different; the raw materials (malt, grain, corn, potatoes, &c.), introduce other ferments which have a very disturbing influence. Already during the germination of the grain we notice that besides the useful diastase, a certain quantity of organic acid is developed. But this is only the beginning of the trouble, for we see this acidity increasing during all the following operations, from the making of the sweet wort to the end of the alcoholic fermentation. This acidity is due chiefly to the formation of lactic and butyric acids, which are the result of the activity of well specified micro-organisms, the lactic and butyric ferments, the latter being more specially known as *Clotridium Butyricum*. If a small quantity of lactic acid seems to be favourable to a healthy development of yeast cells, a too large quantity of this acid is useless if not harmful, and any quantity of butyric acid is decidedly injurious to the enzymatic action of the diastase as well as to the alcoholic fermentation.

Alcohol manufacturers are very cautious to avoid acidification, as they know that the yield of alcohol is smaller in proportion to the increasing acidity of their wort or mash.

The ferments which develop these acids are particularly active at a temperature of from 50° to 60° C. This means that just that temperature which is most favourable for the diastatic action of the malt will also allow the acid ferments to show their harmful action and to develop the largest quantity of lactic and butyric acid. At a higher temperature, however, the action of butyric and lactic ferments is paralysed, and this is the reason why in making sweet wort a temperature is selected whereby the development of acidity is retarded, and by which the diastase does not lose too much of its power. But this means a loss of malt on account of the weakening of the power of the diastase contained in it.

The injurious action of this higher temperature on the diastase is not limited to this; facts have proven that

diastase which has been submitted to a higher temperature, if only for a moment, has been irretrievably injured in regard to its future properties; it will not keep its enzymatic action as long as it would if it had been kept in healthy conditions. This fact is very important if we recollect that the saccharification of the wort is never complete, and that the diastase is expected to continue its action during the whole period of alcoholic fermentation in order to saccharify the last quantities of starch left in the wort. Other means have been tried in order to combat the butyric and lactic bacilli, and the use of sulphuric and muriatic acid, sulphites, and other antiseptics have been proposed. None of them has proved of great advantage; they all show an injurious effect upon the diastatic action of the malt, and the activity of the alcohol ferment.

Hydrofluoric acid or soluble fluorides, on the contrary, when used in very small doses, prevent the development of butyric and lactic acid and are completely harmless to the diastase or to the alcoholic ferment. Furthermore, such small quantities of fluoride, instead of injuring the diastase, seem to excite its activity and preserve its power for quite a longer period than when used alone. Experiments have shown that by addition of a small quantity of fluoride, diastase could be kept in action during seven days, and at the end of this period 80 per cent of the original quantity of diastase was still active, while without the use of fluorides the quantity of active diastase is reduced to 12 per cent at the end of the same period.

No other antiseptics or mineral acids show these preserving qualities when added to diastase. Mineral acids, for instance, when used even in very moderate quantities, have killed the whole of the diastase after five days.

A first advantage of the use of small quantities of fluorides is thus to save malt, of which less need be brought in operation, still giving the same result as larger quantities when used without fluorides. This malt will have a more free and more complete action, and this action will be continued for a longer time on account of the antiseptic properties of fluorides, development of organic acids will be prevented, and the wort can be kept nearer between 50° and 60° C., which is the temperature at which diastase is most active, and where its enzymotic powers are best kept up.

The addition of fluorides have rendered possible the use of malt of very inferior quality with surprising results.

The same beneficial effect of hydrofluoric acid or its salts is observed during the alcoholic fermentation, which thereby becomes more regular and more complete.

The fermentation keeps up with about the same intensity during the whole period until all the saccharine matter has been converted into alcohol. The liquid finally proves to be far less acid than if no fluoride is used. The practical result of all this is a larger yield of alcohol and a better product. If small quantities of fluoride have a beneficial effect on diastase and alcoholic ferment, the contrary result is obtained if larger quantities of fluorine compounds are used. An addition of 25 grms. of commercial hydrofluoric acid (30 per cent) per hectolitre of wort proved very injurious to the action of the diastase, even at temperatures as low as 30° C. At higher temperatures, 55° C. for instance, this injurious effect was already produced by 6 or 7 grms. of hydrofluoric acid per hectolitre. Very concentrated or very acid worts have proved especially sensitive to large quantities of hydrofluoric acid.

The same bad effects of an excess of hydrofluoric acid are shown in the alcoholic fermentation which in some cases may be entirely stopped by it. Soluble fluorides, however, even when used a little in excess, are less violent in regard to this. All this shows that if we have in fluorides a sure and powerful destroyer of useless ferments, this agent should be used judiciously, as any excess of it may prove detrimental to the expected results.

It would be out of the question to give a general recipe

for the quantities of hydrofluoric acid or fluorides which should be used; this depends on too many conditions, such as quality of material, temperature of mashing, concentration or acidity of the wort. For instance, quantities of fluoride which may be advantageous in a wort of average concentration and at a low temperature may become injurious in a more concentrated wort, or if kept at a higher temperature.

In every instance where the fluoride process is introduced in a distillery, some preliminary testing has to be done in regard to this before the best effects are obtained.

The destructive action of fluorides on butyric bacilli in the mash can be easily observed by the aid of the microscope. (See "Das Flüssäure Verfahren in die Spiritus-fabrikation," by Dr. Maerker. Berlin: Verlag von Paul Parey).

The chemical effect of fluorides is better demonstrated by the following experiment (See Soxhlet, *Zeitschrift des Landwirths-Vereins in Bayern*, July, 1890):—1000 grms. of crushed corn were boiled with four litres water and the resulting starch heated in a digester (autoclave) at 3 atm. pressure during one hour. The resulting liquid was cooled off to 50° C., and then 80 grms. of dry malt were added, and the saccharification kept on at this temperature for about thirty minutes. The resulting sweet wort was divided into two equal portions. To one portion 150 m.grms. of ammonium fluoride were added (corresponding to 6 grms. per hectolitre) and the other portion was left as it was. Both portions were kept constantly at 30° C. After two days, the wort without fluoride had considerably thickened and was full of gas bubbles, while the other portion which contained fluoride remained entirely clear and liquid.

A comparative analytical examination of both liquids showed:—

	No fluoride.	Fluoride.
Degrees saccharometer	13'30	13'60
Maltose	10'12	11'61
Dextrin	2'07	1'07
Acidity (normal soda solution per 100 c.c. wort)	8'15	3'9

(To be continued).

ON THE MANUFACTURE OF ALKALINE NITRITES, LEAVING WHITE-LEAD AS A BY-PRODUCT.

By H. N. WARREN, Research Analyst.

THE production of sodium nitrite, which is at present being extensively used as a reducing agent in the arts and manufactures, has of late become the subject of no small amount of research in order to obtain a product of uniform percentage, and at the same time possessing marketable appearance.

The history of white-lead has also been so extensively dealt with in the previous pages of scientific literature that, in order to deal more fully with the subject, or at least in a beneficial manner, presents at once a problem that can only be solved with difficulty.

Sodium nitrite of 98 per cent is at the present time realising £30 per ton, and white-lead £20, but to manufacture these compounds up to the above percentage by any of the ordinary methods, entails considerable expenditure as regards the depreciation of plant, &c., leaving little room for profit; and to avoid these difficulties the author has contrived a method by which galena is caused to act as a reducing agent upon sodium nitrate, yielding at the termination of the reaction sodium nitrite, sodium sulphate, and white-lead. The process, as briefly detailed, is brought about as follows:—

A sufficiency of commercial nitrate is intimately mixed with a sufficiency of ground galena, to which is supplied

an adequate portion of water, and the whole introduced into a capacious leaden retort, after which is added a sufficiency of vitriol. The reaction which is thus afforded terminates with the production of sulphate of lead which remains in the retort; while at the same time the nitrous gases thus freed by the liberated nitric acid coming into contact with the galena are ejected from the retort by blowing in a current of air, and conveyed hence into a solution of soda-ash, thus causing a free evolution of carbonic acid; whilst sodium nitrite remains in solution and requires merely crystallising to render it saleable. The sulphate of lead remaining is next treated with a solution of sodium carbonate and sodium hydrate, and boiled in contact with the same until completely converted into white-lead, requiring only to be dried. As expected, the first samples of white-lead thus produced were entirely useless, presenting no body, and of a very inferior colour; but after a considerable lapse of time, the author has had the satisfaction of preparing by the introduction of certain ingredients not hitherto noted a compound possessed of properties corresponding to the finest prepared Dutch samples, and rivalling the same as regards colour.

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NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 194).

Determination of Lead.

THE decomposition of chromic acid with hydrogen peroxide may also be utilised for the determination of lead, bismuth, and barium,—elements which form with chromic acid compounds insoluble in water. The experiments required have been executed by A. Baumann and G. Hauck.

For the determination of lead the solution is first mixed with sodium acetate, partly to remove any free nitric acid which may be present, and partly to neutralise the acid liberated in the subsequent treatment with chromic acid. The quantity of the sodium acetate to be added depends on the quantity of free acids present. In most cases from 1—2 grms. will be sufficient, but even a large excess of sodium acetate does not endanger the accuracy of the determination.

The liquid is heated to ebullition, and a solution of potassium bichromate is gradually added until the liquid floating above the precipitate is distinctly yellow. Too large an excess of the bichromate is to be avoided. The lead chromate is filtered off and washed with water. The filter is then spread out upon a small glass plate and the precipitate is rinsed with dilute sulphuric acid (applied with a washing-bottle) from the filter directly into the wider space of the gas-generator. From 5 to 6 c.c. of 2 per cent hydrogen peroxide are then introduced into the small glass cylinder of this vessel; the generating vessel is connected with the gas-meter, the two liquids are mixed and shaken in the manner already described after the temperature has become equalised.

The volume of oxygen read off is reduced to 0°, and 760 m.m. atmospheric pressure, and the resulting number is multiplied by 4.9776. The weight of lead oxide sought for is thus obtained in m.grms; for 1 c.c. oxygen equals 4.9776 m.grms. PbO (the atomic weight of Pb = 206.4).

As 1 mol. chromic acid, CrO₃, combines with 1 mol. lead oxide to form lead chromate, and as a mol. chromic acid with hydrogen peroxide evolves 4 atoms of oxygen, 4 atoms of oxygen liberated indicate 1 mol. lead oxide, i.e., 4 × 15.96 parts by weight of oxygen = 222.36 parts

by weight of lead oxide. Thus we obtain the number 4.9776 on the supposition that 1 c.c. of oxygen weighs 1.42908 m.grms.

As it will be seen the gas-volumetric determination of lead depends mainly on the liability of lead chromate to be decomposed by an excess of free dilute sulphuric acid, with formation of lead sulphate, and free chromic acid, which then, with hydrogen peroxide, evolves the quantity of gas corresponding to 4 atoms of oxygen.

It must be mentioned that this decomposition of lead chromate only takes place with the desirable rapidity if the quantity of the precipitate of lead is small. With larger quantities (200 m.grms. lead chromate or upwards) it is well to digest the lead chromate for several hours with dilute sulphuric acid before the volume of the gas is measured. Otherwise in the determination it is necessary to shake for fifteen to twenty minutes until the analysis is complete.

Lead may be determined more simply and quickly by difference with any solution of potassium bichromate (the standard of which may be very quickly ascertained by a gas-volumetric determination), than in the direct manner. The indirect method is therefore to be especially recommended when several analyses have to be executed in succession, or when considerable quantities of lead have to be determined in a liquid.

For effecting the indirect analysis the plumbiferous liquid, which must contain only very little nitric acid in excess, is introduced into a measuring flask containing 100 c.c., diluted with water to about 50 c.c.; sodium acetate is added (about 1 grm.), and it is precipitated in heat with a quantity of potassium bichromate of known strength, very accurately measured with a pipette, so that the supernatant liquid may appear distinctly yellow. It is then allowed to cool, filled up to the mark, filtered through a dry folded filter, and from 30 to 50 c.c., after the addition of 10 c.c. of dilute sulphuric acid, are taken for the gas-volumetric determination. The results obtained by both methods are very accurate.

5. *Determination of Bismuth.*—For the gas-volumetric determination of bismuth the orange-red bismuth chromate, (BiO)₂Cr₂O₇, is most suitable. It is obtained by pouring a solution of bismuth nitrate, as neutral as possible, into a hot solution of potassium bichromate.

The bismuthiferous liquid, which must not contain more than very minute quantities of free nitric acid, must be poured, whilst constantly stirring, into a hot solution of potassium bichromate, taking care that the bichromate remains in slight excess. The precipitate must be thorough of an orange-yellow, and so dense that the supernatant reddish yellow liquid becomes very quickly clear. If the precipitate has more of a yolk of egg colour, a little more of the bichromate solution must be added. The whole is then boiled for about ten minutes, or placed in a boiling water-bath; the precipitate, which deposits rapidly, is washed with hot water by boiling and decantation. Hereupon the bismuth chromate is re-dissolved in a little dilute hydrochloric acid, and the solution is rinsed into the wider space of the gas-generating apparatus. The portions of precipitate which adhere to the filter are easily washed into the generator with dilute hydrochloric acid (as in the determination of lead). Ten c.c. of dilute sulphuric acid (1:5) are added to the chromate solution, from 5 to 10 c.c. of hydrogen peroxide are put into the small glass cylinder, and the chromic acid is determined gas-volumetrically by mixing and shaking the liquids.

As according to the above formula, which may also be written 2CrO₃.Bi₂O₃, 2 mols. of chromic acid come to 1 mol. bismuth oxide, and as the former with hydrogen peroxide yield 8 atoms of oxygen, 8 × 15.96 parts by weight of oxygen = 463.88 parts by weight of bismuth oxide (atomic weight of Bi = 208). Hence it is calculated that 1 c.c. of oxygen evolved at 0° and 760 m.m. barometric pressure represents 5.192 m.grm. bismuth oxide.

In order to find from the volume of oxygen read off the

* *Zeit. für Angew. Chemie and Zeit. für Analytische Chemie*

quantity of bismuth in m.grms., we reduce the volume to 0° and 760 m.m. pressure, and multiply the number obtained with 5.192.

The determination of bismuth, like that of lead, may also be effected indirectly, the bismuth being precipitated in the manner described with a measured excess of bichromate solution of known strength in a 100 c.c. flask, filling up to the mark and determining the chromic acid in a part of the filtrate. The indirect method is more convenient and quicker, as it requires no care in filtering the precipitate, and the washing is dispensed with.

(To be continued.)

THE LAWS AND NATURE OF COHESION.

PART I.

By REGINALD A. FESSENDEN,
Prof. Elect. Engineering, Purdue University, Ind.

DESIROUS of finding some relation between the conductivity of metals and their other physical properties, the writer several years ago began to tabulate all the data he could find. Realising the uselessness of comparing the properties of substances whose natures are essentially different, as wood and iron, it was decided to confine the work to the elementary substances. It was found that the only elements whose properties were at all well known were those of the five chemical groups comprising the following metals:—(I.) iron, nickel, cobalt, platinum, osmium, iridium; (II.) sodium, copper, silver, gold; (III.) magnesium, zinc, cadmium, mercury; (IV.) aluminium, thallium, indium, gallium; (V.) silicon, tin, lead.

The data collected were not very concordant, but when they had been compared and the most probable values taken, laying due stress on the purity of the substances examined and the standing of the observer, various regularities or laws were at once apparent, and it is for the purpose of pointing out one of these that the following paper has been written.

This piece of paper, taken as a whole, has certain properties, a certain size, a certain weight, a certain motion, and is the seat of a certain force which attracts other ponderable bodies to it. A single atom of matter has its weight, motion, size, and force. The weights of the atoms form the basis of stoichiometric chemistry, their motion that of the kinetic theory of heat. To their size less attention has been paid; we have only Mendeleeff's curve and certain experiments of Roberts-Austen, who has shown that the tensile strength of gold is weakened, not in proportion to the weight of the metal alloyed with it, but to the volume, in the same way as ten lumps of gravel weaken a casting more than ten grains of sand. Of the force—the force of cohesion—still less is known, in fact absolutely nothing, and the object of this note is to point out what the nature of this force is and what its laws are.

In its early youth science was riotously extravagant of ethers, and any puzzling phenomenon was considered warrant enough for the creation of a new one. As it has grown older it has grown also more economical, until at the present day the scientist who should ask for an appropriation of a new ether, to help him out of a difficulty, would be frowned upon. For this reason, if no other, we will confine ourselves to examining the various means by which our present ether has been supposed capable of producing the forces which cause cohesion.

1. *Gravitation*.—There have not been wanting eminent scientists who have considered that gravitation could account for cohesion, and there have been many ingenious theories proposed, for instance, that of Watts, who supposed that (since the effects of gravity on the moon's path may be supposed to consist of two parts, one independent of the shape of the earth and varying inversely as the

square of the distance, the other dependent on the shape and varying inversely as the cube of the distance), if the atoms were of irregular shapes it might account for the effects. But no theory with gravitation as its basis will hold; first, because the effects are much too small; second, because, as we shall see, the cohesive force is totally independent of the weights of the atoms and depends on the size only.

2. *Condensation and Rarefaction of the Ether caused by the Motion of the Atoms*.—If we hold a pith ball near a tuning fork the pith ball will be attracted up to a certain distance, and will then be repelled if brought closer. This theory has been a favourite with many, but as such an attraction would vary with the motion of the atoms in a way that we know the force of cohesion does not, it also must be dismissed.

3. *Electricity*.—That the force of cohesion was due to electricity has long been vaguely suspected, on the same principle apparently that electricity was considered to be the cause of life, i.e., "Life is a wonderful thing and unexplainable, electricity is a wonderful thing and unexplainable; therefore electricity is life,"—the argument being possibly aided by an instinctive recollection of the Athanasian creed, which states that "there is only one incomprehensible." The writer is not aware that any evidence in favour of this theory was ever offered, so it was probably merely a guess.

Having rejected theories 1 and 2, we may see how the facts agree with the theory that cohesion is an electrostatic effect.

If we electrolyse a solution of silver nitrate, we know from Faraday's work that every atom of silver deposited on the electrodes carries over a certain quantity of electricity. This quantity is always the same, no matter how or when or where we perform the electrolysis, and this quantity seems to be related to the atoms in the same way as a pint of water to a pint measure. We may calculate the quantity on each atom in the following way. One c.c. of silver weighs about 10.5 grms. One coulomb is carried over by every 1.12 m.grms. of silver deposited, therefore the charge on the atoms contained in one c.c.

of silver is $\frac{10500}{1.12} = 10^4$ coulombs.

As the sizes of the atoms vary from 10^{-7} to 10^{-8} c.m. in diameter, and silver is a small atom ($\frac{1}{2}$ the size of potassium), we may call its size 10^{-8} c.m. In a c.c. of silver then there would be 10^{24} atoms, which would give as the charge on each atom $10^4 \div 10^{24} = 10^{-20}$ coulomb. The capacity of an atom having a diameter of 10^{-8} c.m. is $\frac{10^{-8}}{18 \times 10^{11}} = 0.5 \times 10^{-20}$ farads.

The potential on each silver atom will therefore be about one volt. We may look at the c.c. of silver as being made up of planes, each plane consisting of one layer of atoms. The distance between the centres of any two layers would be 10^{-8} c.m. The potential on the atoms being one volt, the attraction between any two layers would be—

$$\frac{4.5 \times 10^{-11} \times 1^2}{10^{-16}}$$

grms. per c.m.² = 4500 kg. per c.m.² = calculated tensile strength of silver = 45 kg. per sq. m.m.

From Wertheim's results we have:—Observed tensile strength of silver = 38 kg. per sq. m.m. That the calculated and observed results should be so close is, of course, only a piece of good fortune. We have no right to expect it, and the data on which the calculation is based is not known with sufficient accuracy. Still, the result is a remarkable one, and places beyond question the fact that the known electric charges on the atoms can produce effects of the same order as those observed.

Having shown this, we may follow up the theory by investigating in what way the cohesion of the metals would vary if this were the case. Evidently (since every atom, large or small, has the same quantity of electricity,

and the larger the atoms of a metal the farther away the centres of the atoms would be) the cohesive force should be inversely proportional to some power of the size (or atomic volume, as it is called, and which is got by dividing the atomic weight by the density of the substance). The following table shows this to be the case. In the first column are the names of the metals; in the second their relative sizes, or atomic volumes; in the third their rigidity, as given by Mr. Sutherland in the *Philosophical Magazine*, August, 1891:—

I.	II.	III.	IV.	V.
Iron ..	7.1	750×10^9	483×10^9	550×10^9
Copper ..	7.1	430	483	550
Zinc ..	9.2	350	314	340
Silver ..	10.2	280	270	270
Gold ..	10.2	270	270	270
Aluminium	10.4	250	250	260
Magnesium	14.0	150	154	143
Tin ..	16.0	136	122	100
Lead ..	18.0	84	100	83
Cadmium ..	13.0	No data.		170 calculated.

As will be seen, the agreement is perfect, with the exception of iron, and those who are aware how greatly the properties of iron are changed with the least particles of impurity will possibly agree with me in thinking that absolutely pure iron would be less rigid; in fact, some recent experiments show that it is so, being nearer 600 than 750; but I have not inserted this value, because a comparison with a set of observations made by one observer at one time and by one method would have a greater value than comparison with a lot of picked results from different observers.

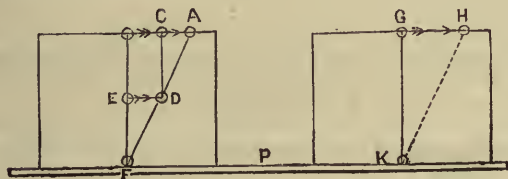


FIG. 1.

FIG. 2.

Assuming the electrostatic theory, we can easily calculate the exact function which rigidity should be of the atomic volume in the following way:—

Suppose Figs. 1 and 2 to represent 2 c.c. of different elements, of which the atoms of one are twice the diameter of the other, or, to put it more accurately, the distance between centres of atoms is twice as great in the one case as in the other. Let x contain the smaller atoms. Suppose one face made fast to the plank, p , and both sheared slightly till they have the position shown by the dotted lines. It is evident that the ratio of work done in bringing the atom at G over to H , to that done in bringing E to D , or C to A , will be the ratio of the force of attraction between K and G to that between E and F . This latter varies inversely as the square of the distance, according to the well-known electrical law; and, consequently, as the distance GK is twice that of EF , the work done in moving E to D will be four times that done in moving G to H . Again, in Fig. 1 there will be 2^3 as many atoms to be displaced as in Fig. 2, so that, on the whole, there will be $2^3 \times 2^3$ as much work done in displacing the cube in Fig. 1 as in Fig. 2. In other words, the rigidity will vary inversely as the fifth power of the distance between the centres of the atoms, or as (atomic volume) $^{5/3}$. Col. IV. gives the results calculated on this theory. As will be seen, they agree fairly well, as well as could be expected, considering the fact that we have left out one factor. This is the variation of rigidity with temperature, and as it would be obviously unfair to compare lead and silver at 600° C., it is obvious that our calculated results should

only be applied when the metals are at some one point, say, at a temperature which is one-fourth the temperature of their melting-point. As those metals having the greatest atomic volume, as a rule, melt at lowest temperature (though there are many exceptions to this) we may make a rough sort of formula, which shall give the rigidity at ordinary temperatures by multiplying again by the atomic radius, so we get (atomic volume) $^{2/3}$ as the rate at which rigidity varies with size of atoms. Col. V. is calculated in this way from the rough formula—

$$\text{Rigidity} = \frac{28 \times 10^{12}}{(\text{atomic volume})^2} \dots \text{Equation I.}$$

The formula for Col. IV., and the more correct one, if we neglect variation of rigidity with temperature is—

$$\frac{12560 \times 10^9}{(\text{atomic volume})^{5/3}} \dots \text{Equation II.}$$

The other moduli are related to that of rigidity. For if we represent Young's modulus by $\frac{Y}{a}$, then the modulus of rigidity is represented by—

$$\frac{Y}{2(a+b)}$$

and the bulk modulus by—

$$\frac{Y}{3(a-2b)}$$

where b represents the lateral shortening accompanying the longitudinal lengthening a . So if b bears to a any constant ratio, then Young's modulus and the bulk modulus will each be some fraction of the modulus of rigidity. The

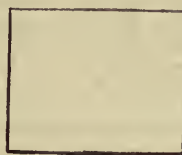


FIG. 3.

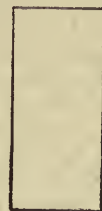


FIG. 4.

Continental writers, at least a good many of them, hold that $\frac{b}{a} = \frac{1}{4}$. Kelvin, Tait, and Stokes say there is no

relation. On the one hand, it is certain that $\frac{b}{a}$ is not constantly equal to $\frac{1}{4}$. On the other hand, it does not follow that there is no relation between the two, and the evidence which has been brought to prove this has no value, for we have no right to argue from the facts that in indiarubber $\frac{b}{a} = \frac{1}{2}$, while in cork $\frac{b}{a} =$, say, $\frac{1}{100}$, that $\frac{b}{a}$ does not have any constant ratio in metals. The laws which govern the moduli of compounds and non-homogeneous substances like indiarubber and cork are not the same as those which govern homogeneous substances like gold and silver.

(To be continued).

Determination of Starch and Action of Dilute Acids upon Cellulose.—M. Guichard.—Various procedures which succeed with free starch are of little or no value with cereals. Cellulose, though it has no rotatory action, acquires such a property by saccharification, and has then an effect upon determinations of starch. Its effects are partly annulled by the inverse rotation due to the nitrogenous substances.—*Bull. de la Soc. Chim. de Paris.*

NOTICES OF BOOKS.

Odorographia: A Natural History of Raw Materials and Drugs used in the Perfume Industry. Intended to serve Growers, Manufacturers, and Consumers. By J. CH. SAWER, F.L.S. London: Gurney and Jackson (Successors to Mr. Van Voorst). 1892. 8vo., pp. 384.

THE sense of smell, though of far greater importance in scientific research than that of hearing, has been strangely neglected. It has not been systematically trained, and no attempts of moment have been made to intensify, direct, or record its indications. For the nose we have nothing at all analogous to the "scopes" and the "phones" with which the eye and the ear are respectively armed. Hence we must warmly welcome a treatise like the present, which, though its main purpose is commercial and industrial, must still help to draw attention to the latent capabilities of this sense.

The author in his introduction very correctly says that no sense is capable of receiving such delicate impressions as that of smell, and that none retains them so permanently. The eye, even with the wonderful aid of the spectroscope, is unable to recognise such delicate distinctions, either qualitative or quantitative, as does that of smell. Mr. Sawyer quotes H. H. Fischer and Pentzoldt, of Erlangen, for the experimental result that air containing

$\frac{1}{23000000000}$ of a m.grm. of mercaptan in a c.c. of air can be recognised. But what of certain insects, e.g., members of the genera *Saturnia*, which can detect the presence of a virgin female of their own species at distances exceeding a mile, even though woods, eminences, houses, &c., intervened? But the delicacy of this sense, even in mankind, is little recognised. It is on record that a little girl, born blind and deaf, and being brought up at an orphan asylum, was employed in sorting the clothes of the children as they came back from being washed. By smell alone she was able to distinguish the socks of the boys from those of the girls!

It must surely make every chemist and biologist crave for the due culture of a sense which, in an unassisted state, can perform such wonders.

The author gives an interesting list of plants which emit powerful, peculiar, and often offensive odours, the cause or the function of which has in many cases not been traced. Here, we cannot help saying, is a field of research open to chemists who have the opportunity of obtaining such plants in a recent condition and in quantity.

The author describes, in successive chapters, organisms which serve as the sources of well-known and admired scents. Foremost come musk and its allies, which are secreted not merely by the musk-deer, the civet, the muskrat, and other mammalian species, but by alligators and certain insects. *Aromia moschata*, a longicorn-beetle, formerly common near Tottenham, but now banished by the encroachments of "Jerry, the builder," is said to emit a strong smell of musk at pleasure.

In the next chapter the author discusses the odour of the rose. This well-known perfume cannot be extracted and concentrated in perfection by distillation, but only by maceration in pure grease followed by "enfleurage."

It is an interesting fact that although vaseline and other mineral fats absorb perfumes very readily they do not retain them, and are consequently of no use for the manufacture of pomades and scented oils. One of the largest firms at Grasse informs the author that purified grease and olive oil are the best materials at present known. Here also is a suggestion for research.

The citrine odours—orange flower, neroli, syringa, gardenia, &c.—form another important type. It is said that Curaçao yields the bitterest of bitter oranges and the sweetest of sweet oranges, but that lemons and limes if planted there turn sweet and die. Here are more problems

The fourth chapter takes up the jasmine type. There are upwards of one hundred species of jasmine known, all save one or two natives of the hottest parts of the Eastern hemisphere. To the same class belong the jonquil, the hyacinth, and the tuberose. Why does the author call this plant *tubéreuse*?

The "odour of the hayfields" seems due to kumarine, which we have transmogrified into "coumarine." Its presence has been traced in *Anthoxanthum odoratum*, in a number of other grasses, in ferns, orchids, in the date-palm, and in other plants belonging to very various orders.

Space does not allow us to prolong our examination of this most interesting work. We notice with pleasure that the author promises a second volume. He does not omit to call attention to the scope for flower-farming in our tropical and sub-tropical colonies.

Notes on Qualitative Chemical Analysis. By P. LAKSHMI NARASU NAYUDU, B.A., Professor of Physical Science, S.P.G. College, Trichinopoly. Madras: K. Murugera Chetty, 1892, 8vo., pp. 122.

WE are exceedingly glad to see our Indian fellow-subjects pressing forward in the study of Science; but we cannot help suggesting that they might employ their time and their abilities better than by compiling elementary manuals. However good they may be the language is overstocked with similar treatises. On the other hand, India abounds in products which have not been thoroughly examined, if at all, and presents numbers of phenomena requiring a closer study. We submit, in all courtesy, that the author might preferably turn his attention to such questions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 14, October 3, 1892.

On Fossil-Wood containing Fluorine.—Dr. T. L. Phipson.—The author examined a specimen of fossil-wood from the Isle of Wight which contained 32.45 per cent of phosphoric acid and 3.90 per cent of fluorine. It seemed to have been fossilised by calcium phosphate and fluor-spar.

Identity of Cascarine with Rhamnoxanthine.—Dr. T. L. Phipson.—The yellow, crystalline substance described by M. Leprince (*Comptes Rendus* of August 1, 1892), as extracted from *Casara sagrada* is identical with the substance which the author extracted from the bark of *Rhamnus frangula*, to which he ascribes in the CHEM. NEWS the composition $C_{12}H_5O_5$. The two substances are alike in their composition and in their reactions.

A Respiratory Globuline contained in the Blood of the Chitons.—Dr. A. B. Griffiths.—The blood of these creatures is yellow, but the pigment is a luteine or lipochrome, and possesses no respiratory function. The blood contains a colourless respiratory globuline containing no metal in its molecule, but possessing the same properties of oxygenation and de-oxygenation as hæmoglobine, hæmocyanine, pinnaglobine, chlorocruorine, &c. The author ascribes to this compound the formula $C_{621}H_{814}N_{175}SO_{169}$. When charged with oxygen it is colourless.

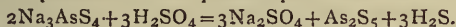
Influence of the Electric Light on the Structure of Herbaceous Plants.—Gaston Bonnier.—In the author's experiments the electric light has been maintained

without ceasing, night and day, for seven months, and if it was desired to try the effects of discontinuous light the plants in question were covered with black screen. Certain plants perished even under an intermittent light; others manifested an exuberant growth with a more intense verdure of the leaves and a deeper colour of the flowers. The modifications are analogous to those which occur in the plants of high latitudes. The structure of the leaves was in some cases modified so that they could scarcely be recognised. Direct electric light is injurious to the normal developments of the tissues, even at a distance of more than 3 metres, in consequence of the ultra-violet rays.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 4.

Apparatus for Obtaining Gases absorbed in Water by a Combination of the Mercurial Pump with Ebullition.—F. Hoppe-Seyler.—This paper requires the accompanying illustration.

Method of Separating Sulpharsenic Acid from Sulphoxyarsenic Acid.—Le Roy W. McCay.—The method is founded on the following facts:—1. If the solution of an alkaline sulpharsenate is distinctly acidified with sulphuric or hydrochloric acid the salt is instantly decomposed, with an escape of hydrogen sulphide and a separation of arsenopentasulphide:—



2. If a highly dilute, strongly refrigerated solution of an alkaline sulphoxyarsenate is slightly acidulated with dilute sulphuric acid, the salt is decomposed and the sulphoxyacid is set at liberty. Under these circumstances it is not decomposed into arsenious acid and free sulphur, but remains quite unaffected. The ice-cold solution remains perfectly clear for hours, and the presence of traces of hydrogen sulphide does not occasion the slightest perceptible decomposition. In order to separate the two acids from each other it is merely necessary to dilute the solution strongly (500 c.c. water to 0.1275 gm. $\text{As}_2\text{O}_3\text{S}_2$), and to refrigerate down to about 0°. On account of a possible gradual decomposition of sulphoxyarsenic acid into arsenious acid and free sulphur, the filtration should be effected as quickly as possible, for which purpose the Bunsen filter-pump is very useful. The following salts were employed:—Bouquet and Clèz's potassium sulphoxyarsenate ($\text{H}_2\text{KAsO}_2\text{S}$), of a high degree of purity, and a sodium sulpharsenate ($2[\text{Na}_3\text{AsS}_4]15\text{H}_2\text{O}$), which gave on analysis 38.07 instead of 38.08 per cent As_2S_5 . In the separation I proceeded as follows:—The salts were dissolved in 500 c.c. of water at the temperature of ice, and the solution was then mixed with a slight excess of dilute sulphuric acid. The bottle containing the solution was set in a mixture of ice, common salt, and water, and a violent current of air was drawn through the liquid for about fifteen minutes. After the air has been shut off and the pentasulphide is deposited, the clear supernatant liquid is decanted off, filtered through a Gooch crucible; the precipitate is placed in the crucible and well washed, first with water and then with alcohol. The precipitate is dried at from 105°–110° until the weight is constant, and it is then extracted from six to eight times with carbon disulphide, washed with absolute alcohol, dried again, and weighed. It has been found that this extraction is essential in order to the 0.001–0.002 gm. of sulphur insoluble in cold alcohol and almost invariably mixed with the arsenopentasulphide. The cold, clear filtrate, which scarcely smells of sulphuretted hydrogen, is treated with chlorine, concentrated to a small volume, and placed in a pressure bottle holding about 200 c.c. The bottle is filled up with water which has been recently boiled, the liquid is treated with a strong current of sulphuretted hydrogen until it becomes opalescent, the stopper is firmly inserted, and the whole is heated for an hour in a boiling water-bath.

The pentasulphide is then filtered off, completely washed with water, and then with absolute alcohol, in order to remove traces of sulphur, dried at from 105°–110° until the weight becomes constant and weighed.

On Iodometry.—Theod. Salzer.—This paper will be inserted in full.

Analysis of Horse-Fat.—C. Amthor and Julius Zinc.—The authors give for the kidney fat of horses the following determinations:—

Specific gravity at 15°	0.9320
Melting-point	39°
Congeaing-point	22°
Melting-point of the fatty acids	36°–37°
Congeaing-point	30°–30.5°
Hegner's number	95.47
Reichert's number	0.33
Saponification number	198.7
Acid number (i.e., m.grm. KOH to 1 gm. fat)	1.73
Acetyl number	6.64
Iodine number	81.09
" " the fatty acids	83.88

The consistence of the fat is that of a soft salve, and its colour is a golden yellow.

Determination of Aluminium Phosphate by Precipitation from its Solutions with Ammonia and Alkaline Acetates.—G. Glaser.—This paper will be inserted at length.

On Boyer's Method of Determining Nitrogen.—C. Arnold and Conrad Wedemeyer (see *Comptes Rendus*, cxiii., p. 5c3).—Already inserted.

An Easy Method of Determining Nitrogen in Nitrates.—C. Arnold and Conrad Wedemeyer.—This paper will be inserted in full.

Action of an Iron Copper Couple upon Nitrates and Nitrites in Sulphuric and Hydrochloric Solutions.—Karl Ulsch.—This memoir is too voluminous for insertion.

Determination of Tartar in Sweet Wines, according to the Method of Berthelot and Fleurien.—Dr. E. Ackermann.—Already inserted.

Attempt at the Detection of Foreign Fats in Butter.—Dr. J. Erdélyi.—The author, after referring to the defects of existing methods, recommends the use of cumol. The clear filtered samples of fat or mixtures of fats are placed for from 24 to 48 hours in an ice-closet. Two c.c. of each are then introduced into dry tubes most carefully cleansed, each of 2c. m. internal diameter; 6 c.c. of cumol are then added to each, and they are allowed to stand at the temperature of a dwelling-room for 24 hours longer. The tubes, along with thermometers, are then surrounded with crushed ice for one hour, and are then lifted out for a moment for examination at certain intervals of time. Their clearness or turbidity in certain times characterise the fats.

Apparatus for the Uniform Mixture of Large Quantities of Pulverulent Substances.—C. Mann.—This paper requires the two accompanying figures.

Self-Acting Filtration Apparatus.—Prof. F. Albin Hoffmann.—This paper cannot be intelligibly reproduced without the illustration.

Detection of Salicylic Acid in Salicylaldehyd and in Salicylic Methyl ester.—A. Schneegans and J. E. Gerock (*Journ. d. Pharm. von Elsass-Lothringen*).—The authors utilise the circumstance that the well-known violet colour which the above compounds produce with ferric salts is permanent on shaking with ether only in case of salicylic acid, whilst in the aldehyd and ester it disappears. Chloroform, amyl alcohol, acetic ethylester, carbon disulphide, petroleum ether, paraffin oil, benzene, toluene, xylene, and pure acetone act similarly to ether. The sensitiveness of the salicylic acid reaction is not impaired by the presence of aldehyd or ester.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., No. 14.

On a Tetramethylmetadiamidic Benzidine.—Ch. Lauth.—This compound, $C_{16}H_{22}N_4$, is a colourless base which crystallises in long needles; it is very soluble in hot benzene and alcohol, from which it is almost entirely deposited on cooling. Boiling water dissolves it very slightly. Its sulphate, hydrochlorate, nitrate, and acetate are very soluble in water. With ferric chloride it gives a colour which is first orange and then brown; with lead peroxide, in presence of acetic acid, a yellowish brown colour; with bichromates a bright orange; with nitric acid a fine violet, changing to a brown.

The Complete Elimination of Barium in Salts of Strontium.—MM. Barthe and Falières.—The authors reply to the criticism of J. Cannepin on their process; the latter seeks to maintain that barium sulphate precipitates strontia from its saline solutions, and takes its place so as to yield a soluble barium salt.

The Calorific Power of Coal and the Formulæ used for its Determination.—M. Scheurer-Kestner.—The author asserts that there are coals the combustion-heat of which exceed that of their elements, though they are uncommon.

The Analysis of a Ferruginous Sulphated Water named "de Roufague" found on the Territory of Colliorre in the Eastern Pyrenees.—J. Ch. Essner.—A paper of no general interest.

A Study on the Constitution of Milk, its Acidity or Alkalinity.—L. Vaudin.—The milk of mammalian animals has an acid reaction at the moment when it issues from the teat. The value of the acidity of normal milk yielded by females of one and the same species is relatively little variable. All influences which may occasion a disturbance in the secretion (gestation and parturition, regimen, nature of the soil, &c.), occasion a modification in the acidity. The acid reaction of milk is mainly due to the proteic matters present. The variations of acidity which occur in the course of lactation depend on modifications which occur simultaneously in the nature and the relative proportions of the various proteic matters and of the mineral elements of milk.

Alcoholometers of Precision.—J. A. Müller.—The author finds that certain alcoholometers under official control, and guaranteed as exact by dealers, indicate as a mean 0.2 to 0.3 per cent less alcohol than the quantity deduced from the densities.

The Application of Metaphosphoric Acid to the Separation of the Albumenoids of Milk to the Determination of Lactose.—G. Denigès.—This paper does not admit of useful abstraction.

Specific Determination of Xylose.—G. Bertrand.—Already inserted.

Action of Nitric Oxide upon the Metals and the Metallic Oxides.—Paul Sabatier and J. B. Senderens.—Already inserted.

A New Gas-Volumeter.—J. A. Müller.—An intelligible reproduction of this paper is not practicable without the accompanying figure.

Action of Sulphur in Presence of Water upon the Polybasic Acids.—J. B. Senderens.—Already inserted.

Preparation of Methylbenzoylanilide.—J. Dupont.—The author heated in an alcoholic solution equivalent parts of benzoylanilide potassa and methyl anilide. The methyl iodide has certainly been saponified, but the benzoylanilide had remained absolutely unaltered.

Chemical Constitution of Camphor and of Oil of Turpentine, as well as of their Principal Derivatives.—L. Bouveault.—This lengthy paper does not admit of useful abstraction.

Aniselines, Novel Colouring-Matters.—P. Monnet.—Already noticed.

Cryoscopic Studies in the Benzenic Series.—J. Hausser.—The author has studied the sulphonic acids of benzene from the cryoscopic point of view, and has recognised that these acids have in water molecular depressions different from those of the greater part of other organic substances. The constant 19 of organic substances found by Raoult with very rare exceptions does not exist for these bodies.

Action of Potassium Permanganate upon Organic Acids. Production of New Manganic Salts.—Aug. Lumière and Alph. Seyewetz.—This paper will be inserted in full.

The Chloro-Derivatives of the Isobutylamines.—A. Berg.—The author has studied monochloroisobutylamine, dichloroisobutylamine, and chlorodiisobutylamine.

Action of Alcoholic Soda upon Chlorodiamylamine and Chlorodiisobutylamine.—A. Berg.—An examination of amylamylidenamine and isobutylisobutylidenamine.

New Process for Obtaining the Cyanamides.—A. Berg.—The author has obtained diamyl- and diisobutylcyanamide by causing potassium cyanide to act upon the chloro-derivatives of diamylamine and diisobutylamine.

Transformation of Gallic Acid into Pyrogallol.—Melting-Point of Pyrogallol.—P. Cazeneuve.—If we add to gallic acid double its weight of aniline, the mixture, which is at first liquid, solidifies abruptly with a rise of temperature. There is formed, doubtless, aniline gallate. If the mass is heated we observe at about 120° a regular development of carbonic acid without appreciable rise of temperature. At this temperature the whole of the gallic acid may be decomposed. On heating to 180° and cooling, aniline pyrogallate is obtained in long crystalline needles very instable. Most of the liquid aromatic amines form an equally favourable medium for the transformation of gallic acid. The melting-point of pyrogallol is 132° (not corrected), and not 115° as asserted in the text-books.

MEETINGS FOR THE WEEK.

FRIDAY, 28th.—Physical. (1) Discussion of Mr. Williams's paper on the "Dimensions of Physical Quantities." (2) Discussion of Mr. Sutherland's paper on the "Laws of Molecular Force," to include papers by Dr. Young and Mr. Thomas on the "Determinations of Critical Density, Critical Volume, and Boiling-Points."

TO CORRESPONDENTS.

R. H. Laverick.—We would suggest inspissation of the juices at a low temperature under reduced atmospheric pressure, or perhaps preferably in a current of hydrogen or nitrogen.

N. P. Martin.—Consult a memoir on "Analysis of Alloys containing Copper, Zinc, and Nickel," by Thomas Bayley (*Phil. Mag.* July, 1878), or, "Brannet's Metallic Alloys," 1889.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1718.

VANADIFEROUS LIGNITE FOUND IN THE ARGENTINE REPUBLIC, WITH ANALYSIS OF THE ASH.*

By JOHN J. J. KYLE, Sc.D.,

Professor of Chemistry in the University of Buenos Ayres;
Assayer to the Argentine Mint.

By order of the Minister of the Interior of the Argentine Republic, the Director of the National Board of Works forwarded to the author a small sample of coal taken from a seam recently discovered near the town of San Raphael, in the Province of Mendoza, with instructions to analyse the mineral and to report on its value as a combustible.

The coal is lustrous, black, even when finely pulverised, without fibrous structure, and remarkably brittle. On being heated it softens, emits much gas, which burns with a smoky flame, yielding a light spongy coke, which after combustion leaves a singularly small amount of a greenish coloured ash. The condensed products of its distillation have an acid reaction. The specific gravity of the mineral = 1.173. Its proximate analysis gave:—

Loss on drying at 100°	..	2.05
Volatile matters ..	..	49.51
Fixed carbon ..	..	47.81
Ash ..	..	0.63

100.00

In the elementary analysis, the carbon and hydrogen were determined by combustion with lead chromate; the nitrogen by combustion with soda-lime, and the sulphur by Eshka's method. Its composition, deducting hygroscopic water and use, was found to be as follows:—

Carbon ..	..	60.59
Hydrogen ..	..	8.63
Nitrogen ..	..	1.43
Sulphur ..	..	4.23
Oxygen ..	..	25.12

100.00

In the calorimetric assay by Berthier's method 1 grm. was found to reduce 23.102 grms. of lead = 5405 heat units. Judging from the above analyses the mineral would appear to resemble most of the bituminous lignites or tertiary coals which occur in this Republic and in Chile. These, however, generally contain a high percentage of ash, the sulphur being chiefly present as iron pyrites. It is evident that such is not the case in the San Raphael mineral, as the percentage of ash is very low, and as will be seen from the analysis later on, this only contains a small proportion of iron oxide. The sulphur determination was carefully repeated with every possible precaution to avoid error, such as might occur from impurity in the reagents, the crucible being heated by an alcohol flame. It would therefore appear that the sulphur must for the most part be present either in the free state or in some form of combination with the organic elements.

The remarkably small percentage of ash and its peculiar greenish colour naturally attracted my attention. On treating it with hydrochloric acid there appeared a deep red colouration, which, on dilution and heating, changed to a greenish blue. On addition of ammonia in

excess the colour disappeared, showing it had not been due to traces of copper, as I had at the first supposed. On further investigation I satisfied myself that the ash contained *vanadium*, and was induced to continue its study as thoroughly as might be possible, considering the small quantity (about 500 grms.) of raw material at my disposal. The mineral was incinerated in a platinum dish over a Bunsen flame, and the ash, still retaining some carbon, was reserved for analysis. The qualitative analysis showed it to contain:—

Soluble in water—

Ca, K, Na, V_2O_6 , SO_3 , and Cl (trace).

Soluble in HCl—

Fe, Al, Ca, Mg, V_2O_5 , Ph_2O_5 , SO_3 and Mn (trace).

Insoluble in HCl—

SiO_2 , Al, Fe, Mg, Ca (trace), and carbon.

In the course of the qualitative examination I had abundant proof that the ash contains a large proportion of vanadium, so that the quantitative methods required to be carefully chosen, to avoid waste of the very limited supply of material, and at the same time secure completeness and accuracy in the results.

The following plan was adopted, in the description of which I shall omit unnecessary details. I have been much indebted to a paper by Dr. Adolfo Doering on the "Separation and Quantitative Estimation of Vanadic Acid," published in the *Boletín de la Academia Nacional de Ciencias en Córdoba, Rep. Arg.* (vol. v., p. 117), and have taken advantage of the author's suggestions with regard to the separation of vanadic acid from iron and alumina and its precipitation as mercurous vanadate.

One grm. of the ash was repeatedly digested in hot dilute nitric acid; the insoluble silicates and carbon were washed on a tared filter, dried at 120°, weighed, ignited to remove carbon, and the weighed silicates reserved for further investigation.

The nitric solution, after removal of excess of acid, was nearly neutralised by sodium carbonate, acetate of sodium added, and, on boiling, iron and aluminium phosphates and vanadates were thrown down. The precipitate was dissolved in nitric acid, some sodium phosphate was added, and the phosphates again precipitated by sodium acetate, the vanadium being retained in solution. The mixed phosphates were collected and weighed, the iron contained in these converted into sulphide, and weighed as peroxide. The phosphoric acid was estimated and its amount *plus* that of the iron oxide deducted from the weight of the total phosphates, the difference being regarded as alumina. As the determination of the Ph_2O_5 included part derived from the added sodium phosphate, that corresponding to the ash was separately determined. The filtrate containing vanadium and excess of sodium phosphate was precipitated by ammoniacal magnesium nitrate, and as the precipitate retained some V_2O_5 it was re-dissolved, and the treatment repeated until the magnesium and ammonium phosphate was colourless, the mixed filtrates containing the V_2O_5 were acidified with acetic acid, and the V_2O_5 precipitated by mercurous nitrate. The mercurous vanadate was washed with hot water, collected, and carefully ignited to expel mercury, the residue = 0.034 grm. V_2O_5 .

The filtrate from the mixed precipitates of phosphates and vanadates, thrown down by sodium acetate as previously mentioned, was nearly neutralised by sodium carbonate, and the V_2O_5 precipitated in the hot liquid by mercurous nitrate; the mercurous vanadate on ignition weighed 0.250 grm. On fusion with sodium carbonate and digestion of the melt with hot water, there remained a residue which weighed 0.008 grm., which being deducted = 0.242 grm. V_2O_5 , not combined with iron and alumina. After getting rid of excess of mercury by H_2S , the filtrate on being neutralised with ammonia assumed a dark colour, and after repose there was formed a very slight precipitate which contained traces of vanadium and manganese sulphides, which were not estimated; the filtrate from

* Read before the British Association, Edinburgh Meeting, 1892.

these was treated by ammonium oxalate, and the lime estimated as usual; traces of magnesia were found in the filtrate but not estimated.

It being now apparent that only a small fraction of the vanadium was in combination with iron or alumina, I treated a fresh portion of ash by digestion in warm ammonia solution, so long as anything appeared to dissolve. The alkaline solution was evaporated in a tared capsule, the residue consisting of calcium sulphate, ammonium vanadate, and vanadates of the alkaline metals. By drying and weighing the residue insoluble in ammonia, which was collected on a tared filter, the amount soluble in ammonia was ascertained. The filter was then ignited and the residue weighed, thus controlling the previous carbon determination. The residue was digested in hot nitric acid and the solution employed to determine the phosphoric acid by means of molybdate of ammonium.

The mixed vanadates and calcium sulphate left on evaporation of the ammoniacal extract were treated with hot water, much of the calcium sulphate remaining undissolved; the V_2O_5 was precipitated by lead acetate, the precipitate collected on a tared filter and washed with hot water, a few drops of ammonium acetate being added to insure removal of any lead sulphate; the lead vanadate was dried at 100° and treated as recommended by Roscoe (Roscoe and Schorlemmer, "Treatise on Chemistry," Vol. ii., Part II., p. 299). As in this method the V_2O_5 is estimated by difference between the weight of the dried lead vanadate and the contained lead weighed as sulphate, the estimation was checked by titration with permanganate of the sulphuric solution, the V_2O_5 having been reduced to V_2O_4 by sulphurous acid. After removal of the excess of lead in the filtrate from the lead vanadate, and of the lime by ammonium oxalate, the filtrate was evaporated to dryness, ignited to expel ammonia salts, the residue moistened with sulphuric acid, again ignited, and the sulphates weighed. The residue dissolved completely in water, the contained SO_3 was on estimation found to correspond to the sulphates regarded as potassium sulphate; the sodium revealed by the spectroscope was therefore a mere trace. As the ash contained no carbonate the lime was calculated as sulphate.

The insoluble silicates were fused with alkaline carbonates, and the melt, being practically free from vanadium, was treated as usual for the estimation of silica and bases.

The composition of the ash after deduction of the carbon (which two separate determinations had shown to amount to 27.8 per cent in the ash as analysed) may be stated as follows:—

Soluble in acid.	Vanadium pentoxide	38.22
	Phosphorus pentoxide	0.71
	Sulphuric anhydride	12.06
	Calcium oxide	8.44
	Ferric oxide	4.98
	Aluminium oxide	3.32
Insoluble in acid.	Potassium oxide	1.73
	Silicic anhydride	13.70
	Ferric oxide	9.42
	Aluminium oxide	5.26
	Magnesium oxide	0.83
Undetermined traces of manganese, magnesia, chlorine, and loss in analysis		1.33
		100.00

As the analysis of the extract obtained by digesting the ash in hot ammonia water showed that, of the total V_2O_5 , viz., 38.22 per cent, no less than 30.6, say 80 per cent, exists either as a vanadium oxide or as a soluble alkaline vanadate, only the remaining 20 per cent can exist in combination with iron and alumina. I have examined the ash under the microscope, and find it made up of particles having by reflected light the colour of unburnished gold; others are translucent and of a greenish white colour; a few are dark red, and have a metallic

lustre. When heated on platinum foil to the highest temperature of the blowpipe flame, the ash undergoes partial fusion, and acquires a dark red colour and metallic lustre.

On being boiled with distilled water, a yellow solution is obtained, the yellow colour being probably due to the change of the potassium metavanadate into tetravanadate, by far the larger part of the vanadium compounds remaining insoluble in pure water, although, as previously mentioned, readily soluble in hot solution of ammonia.

There appears to be no doubt that the ash contains the vanadium, chiefly as vanadic pentoxide, in a free state, partly as potassium vanadate and also some as iron or aluminium vanadates.

From the foregoing it is evident that the San Raphael coal is one of great interest, being not only of fair quality as a combustible, but being also available as a source of vanadic acid for industrial purposes, seeing that each ton of the mineral, supposing it to be equal to the sample, will produce over 14 lbs. of pure ash containing $4\frac{1}{2}$ lbs. of the vanadic pentoxide, of which $3\frac{1}{2}$ lbs. may be extracted by simple treatment of the ash with an alkaline liquor, whilst the remainder is of course susceptible of extraction from the insoluble part as in the case of the basic slags of Creusot (*Compt. Rend.*, xcvi., 42—44), which contain but 1.5 per cent.

In short, the ash of the San Raphael lignite is, so far as my knowledge goes, the richest known material utilisable as a source of vanadium compounds. I have taken steps to obtain information regarding the carboniferous strata whence any sample of mineral was derived; the details cannot fail to be of great interest. Meanwhile I have been assured that the seam where explored is about one metre in thickness.

The Argentine provinces of Cordoba and San Luis are already well known as sources of vanadium minerals, such as vanadite, Descloisite, and psittacinite; the province of Mendoza must now be added to the list of localities in the Argentine Republic where is to be found vanadium.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 206).

Determination of Barium.

THE determination of barium in the manner given for lead and bismuth presents certain difficulties, as on precipitating a neutral solution of barium chloride with potassium bichromate, hydrochloric acid is set free and holds barium chromate in solution. If the precipitation is effected with neutral potassium chromate, the barium precipitate always carries down along with it some potassium chromate, which can not be removed by washing without much difficulty. On the contrary, ammonium chromate appears very suitable. It was first proposed by P. Schweizer for the precipitation of barium, and has since been recommended by R. Fresenius.

For effecting the direct determination the solution of barium is heated to ebullition in a beaker, and a solution of neutral ammonium chromate is then added until the supernatant liquid has a distinct yellow colour. The precipitated barium chromate is filtered off, the portions adhering to the glass and the precipitate itself are washed with dilute ammonium chromate, and a strongly dilute solution of ammonia is ultimately used for washing out the barium chromate. The portions adhering to the beaker are dissolved in a little dilute hydrochloric acid, and the precipitate itself is rinsed with strongly diluted hydrochloric acid (1:20), heated to about 60° , into the external space of the gas-generator. In this manner, the

* *Zeit. für Angew. Chemie* and *Zeit. für Analytische Chemie*.

total quantity of the barium chromate is generally dissolved. Ten c.c. of sulphuric acid are then put in the outer space of the developing-vessel, and the free chromic acid is then determined with hydrogen peroxide in the ordinary manner.

The composition of barium chromate is analogous to that of lead chromate. Consequently four atoms of oxygen evolved correspond to 1 mol. baryta, or 4×15.96 parts by weight of oxygen represent 152.82 parts by weight of BaO ($\text{Ba} = 136.86$). Hence it is calculated that 1 c.c. of oxygen at 0° and 760 m.m. barometric pressure indicates 3.42 m.grms. baryta.

The indirect method which leads more quickly to a conclusion is effected in a quite similar manner. We precipitate in a 100 c.c. measuring flask with an accurately measured quantity of a neutral solution of ammonium chromate, the standard of which has been determined by gas-volumetry, fill up to the mark when cold, filter, and determine the chromic acid which has remained in solution in an aliquot part of the filter.

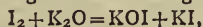
The authors have obtained very satisfactory results in this manner.

Baumann has founded other methods for quantitative analysis upon the behaviour of hydrogen peroxide with iodine. It is already known that oxygen is evolved on the contact of hydrogen peroxide and iodine in an aqueous and acid solution. This reaction does not ensue according to the equation $\text{I}_2 + \text{H}_2\text{O}_2 = \text{O}_2 + 2\text{HI}$; but a simple experiment shows that iodine in water, like manganese dioxide in water and potassium bichromate in a neutral solution, is capable of decomposing a large quantity of hydrogen peroxide without itself undergoing any essential change. Hence this reaction cannot be utilised for the determination of iodine.

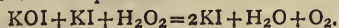
Iodine in an alkaline solution behaves quite differently with hydrogen peroxide. If we dissolve iodine in a cold, saturated lye of potassa or soda there is formed, according to the general assumption, alkali iodate. According to C. F. Schönbein and Berthelot there is formed in analogy to the action of chlorine and bromine alkali hypoiodite.

If upon a solution of iodine in potassa-lye we pour hydrogen peroxide shortly after the reaction of the two substances has commenced, there sets in brisk effervescence in consequence of the escape of oxygen, and the liquid, previously yellow, becomes suddenly colourless. Hence it appears that there was present in the solution not potassium iodate, but a hypoiodite, which like the hypochlorites evolves oxygen.

Iodine, therefore, quite like chlorine, reacts with potassa-lye according to the following equation—



and the decomposition of the compounds formed takes place like the decomposition of chloride of lime—



According to theory, therefore, 2 atoms of oxygen are liberated to 2 atoms of iodine in a watery as well as in an alkaline solution.

In quantitative experiments, however, there is always rather less oxygen evolved than theory requires according to the above equations. This deviation is explained by the instability of potassium hypoiodite. When working with the azotometer the gas-generating apparatus must always be placed in water of the temperature of the room before the commencement of the analysis, so that the rise of temperature which occurs during charging and closing the apparatus may be again equalised. During this short time a part of the potassium hypoiodite passes into potassium iodate and thus escapes determination.

In order to abridge as far as possible the time of the action of the potassa-lye upon the iodine, Baumann brought strongly alkaline hydrogen peroxide in contact with neutral solution of iodine. In these experiments there were obtained to 126.54 parts of iodine exactly 15.96 parts of free oxygen, or exactly the quantity which

the above equations require. Baumann takes this reaction as the basis of the following methods.

Determination of the Free Iodine.

We place in the wider space of the gas-generating apparatus the solution of iodine in potassium iodide, the volume of which must amount to from 40–50 c.c. We allow at first 5 c.c. of hydrogen peroxide (containing about 2 per cent H_2O_2) to flow into the inclosed glass cylinder, and afterwards 10 c.c. of a solution of potassa hydrate (prepared by dissolving 1 part of potassium hydroxide in 2 parts of water). A sufficient inter-mixture of the decomposition liquid is effected spontaneously as the heavy solution of potassa is poured upon the hydrogen peroxide.

After the generating-vessel is closed, and the elevation of temperature has been effected in the known manner, water is allowed to flow down from the measuring-tube, and the liquid in the generating-vessel is set in rotatory motion, with the precaution that none of the decomposition liquid is spilt out of the cylinder.

When the solution of iodine is in rapid motion we suddenly mix the two liquids without interrupting the rotatory movement, and shake vigorously as long as an increase of gas is perceptible in the burette. The chief volume of the oxygen is evolved forthwith in the first seconds, and the decomposition is quite complete if we continue shaking for a minute.

If whilst shaking we avoid touching the sides of the vessel with the hand (which is easily effected), the volume of gas may be read off at the expiry of five minutes, since the reaction takes place with a quite unimportant change of temperature. It is not advisable to wait longer than from thirty to forty minutes, since during this time not only the temperature of the water in the cooling vessels may vary, but frequently a slight escape of oxygen may become perceptible, occasioned by a gradual decomposition of the hydrogen peroxide in the alkaline solution. If we omit to set the solution of iodine in brisk circular movement before decomposition, we must expect to find a loss of oxygen of 0.8 c.c. or 1 m.grm., even though the results are sometimes accurate on mixing slowly and using very dilute solutions of iodine. A loss is also frequently experienced if the iodine is dissolved in a smaller quantity of liquid than the instructions demand. If we use the potassa-lye much more dilute than it is indicated above we obtain too high results, as the hydrogen peroxide sets up a decomposition of the iodides formed, with development of oxygen.

The volumes of gas read off are reduced to 0° and 760 m.m. atmospheric pressure, and the product is multiplied by 11.33. Thus we obtain the weight of the iodine in m.grms., as 1 c.c. oxygen at 0° and 760 m.m. atmospheric pressure corresponds to 11.33 m.grm. iodine ($\text{I} = 126.54$). Perfectly accurate results are obtained by following the simple directions given.

This method may be advantageously utilised for standardising solutions of iodine, since, according to Baumann's experiments, iodine can be determined gas-volumetrically with as much accuracy as by titration with sodium thiosulphate and starch-paste. The gas-volumetric method can be completed in a shorter time and does not require the use of the balance.

In order to determine the standard of a solution of iodine, which approximates to a decinormal, we place 40 or 50 c.c. accurately measured in the external space of the gas-developing apparatus, pour the decomposing liquid into the small glass cylinder, and after the temperature has become equalised, shake with the precautions given above. Of more dilute solutions of iodine we use from 60 to 80 c.c.

(To be continued.)

The Chemical Society.—In consequence of the alterations in the rooms of the Chemical Society, the first Ordinary Meeting of the Society will not be held until Thursday, November 17, at 8 p.m.

ON THE REACTIONS OF FERRIC SALTS
WITH SULPHOCYANATES.

By H. M. VERNON, B.A.

(Concluded from p. 203).

The Effect of Temperature on Ferric Sulphocyanate Solutions.

THE effect of the increase of temperature on the various solutions of ferric sulphocyanate was then determined. The method of procedure was the same as that described by the writer in the paper before alluded to; colour determinations being made at 60°, 50°, 40°, 30°, and 20°. The colour effect at 20° was always taken as 100, and the values at other temperatures compared against this. The colour effects of the solutions were always taken at 20°, both before and after heating. The values were the same to within two per cent, so no chemical change was caused in the solution by the heating.

The effect of temperature on the colour of solutions of the various sulphocyanates with 100 equivalents of ferric chloride was first determined. The solutions examined were at dilutions of 160 litres. From the table it will be seen that the colour increase on rise of temperature is about the same for all sulphocyanates. The experimental error in these determinations is considered at about 3 per cent, and none of the numbers differ by more than this amount from the mean values at each temperature.

A similar series of determinations was made with ferric chloride replaced by ferric sulphate. Here the colour effect, instead of increasing on rise of temperature, decreases considerably. This contrary effect is evidently due to the reaction of the acid sulphates formed in the solution, the quantities of which change on variation of temperature. Thus, Ostwald found ("Lehrbuch," ii., 785) that the affinity of sulphuric acid for soda, compared with that of nitric or hydrochloric acid, decreased from 100 at 20° to 82.7 at 60°. The mean value of the colour effects of the various sulphocyanate solutions at 60° is 81.2, but the similarity of these numbers is probably only accidental. The colour effects of the various solutions show greater variations among themselves than those with ferric chloride, the differences being too great to be due merely to experimental error. We should, in fact, expect them to vary slightly with the different sulphocyanates used, as Ostwald has shown that the relative affinity of sulphuric acid to that of nitric or hydrochloric acids varies with the nature of the base.

The colour of a solution of potassium sulphocyanate and ferric nitrate is affected by temperature to the same extent as solutions of ferric chloride and sulphocyanates. The solution of ferric tartrate and lithium sulphocyanate

decreases in colour effect to a much greater extent on heating than ferric sulphate solutions, and even slightly more than a solution of ferric citrate and potassium sulphocyanate. If the lithium salt had been replaced by the potassium salt, the colour decrease would have been about the same as for the citrate. It was not possible to determine the effect of temperature on a solution of ferric acetate and sulphocyanate, as on heating it decomposed, with precipitation of ferric oxide. We see therefore that sulphocyanate solutions reacting with ferric chloride and nitrate, salts of monobasic acids, show considerable increase of colour on heating, whilst with solutions of ferric sulphate, tartrate, and citrate—salts of polybasic acids—show considerable decrease of colour effect on heating.

As the solutions of ferric sulphocyanate become more dilute, or when less ferric salt is present—that is to say, when the ferric sulphocyanate is present in a more unstable state—the tendency is for the colour effect to decrease on rise of temperature. Thus a solution of potassium sulphocyanate and 100 equivalents of ferric chloride at 800 litres dilution shows only half as much increase in colour effect on heating to 60° as the same solution at 160 litres dilution. A similar solution, with the ferric chloride replaced by the sulphate, shows more than twice as great a decrease of colour on heating as the solution at 160 litres dilution. A solution of calcium sulphocyanate and ferric sulphate at 800 litres, though affected considerably more than at 160 litres, is nevertheless not so much influenced as the potassium sulphocyanate and ferric sulphate solution. The solution containing equal equivalents of ferric chloride and potassium sulphocyanate decreases considerably in colour on heating, whilst a similar solution with ferric sulphate is affected to a still greater extent. The colour effect of this solution could not be determined at 50° and 60°, as it began to decompose and became milky; at 45° the colour effect was 40.6.

On heating a solution of a sulphocyanate and the ferric salt of a monobasic acid, as ferric chloride, there must be two influences at work: one causing the colour effect to increase on heating; the other, to decrease. The increase of colour is probably due to the formation in the hot solutions of anhydrous molecules of ferric sulphocyanate, with increase of colour effect. The decrease of colour is probably due to the water having a greater decomposing effect on the unstable ferric sulphocyanate molecules, owing to its greater activity and molecular motion in hot solutions. As has been shown, in the more dilute solutions, or in solutions containing less excess of ferric salt, the decrease of colour influence counteracts and at last overpowers the increase of colour influence. In solutions of ferric salts of polybasic acids there is still another influence at work, namely, the decrease of colour on heating due to the formation of the acid sulphate, tartrate, or

Reacting salts.	Equivalents of ferric salt to 1 equivalent sulphocyanate.	Dilution in litres.	Colour effect at			
			30°.	40°.	50°.	60°.
KSCN.Fe ₂ Cl ₆	100	160	107.8	116.3	127.5	141.0
NH ₄ SCN.Fe ₂ Cl ₆	100	160	107.7	118.3	131.8	144.0
NaSCN.Fe ₂ Cl ₆	100	160	106.8	113.8	132.4	146.3
LiSCN.Fe ₂ Cl ₆	100	160	105.2	114.8	124.8	138.2
Ca(SCN) ₂ .Fe ₂ Cl ₆	100	160	104.1	115.6	124.4	141.3
Ba(SCN) ₂ .Fe ₂ Cl ₆	100	160	107.0	118.0	127.8	141.4
KSCN.Fe ₂ (SO ₄) ₃	100	160	95.7	90.8	88.2	85.4
NH ₄ SCN.Fe ₂ (SO ₄) ₃	100	160	95.2	92.3	89.6	85.1
NaSCN.Fe ₂ (SO ₄) ₃	100	160	92.9	87.8	84.2	78.2
LiSCN.Fe ₂ (SO ₄) ₃	100	160	93.5	87.0	80.5	75.0
Ca(SCN) ₂ .Fe ₂ (SO ₄) ₃	100	160	95.0	89.0	84.6	80.4
KSCN.Fe ₂ (NO ₃) ₆	100	160	107.6	119.2	128.2	139.8
LiSCN.Fe ₂ (C ₄ H ₄ O ₆) ₃	100	160	83.0	69.2	57.7	48.2
KSCN.Fe ₂ (C ₆ H ₅ O ₇) ₂	100	160	88.0	75.1	63.8	50.5
KSCN.Fe ₂ Cl ₆	100	800	105.4	110.1	112.5	117.9
KSCN.Fe ₂ (SO ₄) ₃	100	800	78.2	65.1	55.5	47.9
Ca(SCN) ₂ .Fe ₂ (SO ₄) ₃	100	800	85.6	74.2	67.1	61.1
KSCN.Fe ₂ Cl ₆	1	80	80.2	68.1	52.6	46.8
KSCN.Fe ₂ (SO ₄) ₃	1	80	78.4	55.8	—	—

citrate, as the case may be. Even in concentrated solutions these two decreasing colour effect influences overpower the influence tending to increase the colour effect.

The Effect of Free Acid on Ferric Sulphocyanate.

When a solution of ferric nitrate was prepared, a small quantity of free nitric acid had to be added to bring up the proportion present in the solution to the amount required by the formula $\text{Fe}_2(\text{NO}_3)_6$. It was thought interesting to determine the effect of the further addition of free nitric acid on the colour of a solution of ferric nitrate and potassium sulphocyanate. The results obtained were as follow :—

Equivalents of HNO_3 added.	1 : 1 Solution, 40 litres dilution.	1 : 1 Solution, 160 litres dilution.	1 : 100 Solution, 160 litres dilution.
0	100	100	100
0.1	109.1	134.5	103.6
0.2	116.2	161.4	104.8
0.5	117.4	207.5	105.7
1	117.2	228.4	106.0
2	111.4	228.7	106.0
3	109.8	222.2	—
5	103.9	206.2	—
10	102.2	176.9	—
20	98.1	152.6	—
30	96.0	146.0	—

The numbers in the first column represent the number of equivalents of acid added, compared with the number already present in the solution. Thus to the solution containing 100 equivalents of ferric nitrate, a hundred times as many equivalents of acid would be added as to an equal equivalent solution. The effect of dilution caused by the water added with the nitric acid was, of course, allowed for. As with the heating of a ferric sulphocyanate solution, the effect of the addition of nitric acid is twofold : on the one hand, it causes an increase of colour effect by causing the ferric sulphocyanate to exist in a more stable or less dissociated state ; on the other hand, it also dissolves or decomposes some of the salt. On addition of free acid to a certain degree, therefore, the colour effect increases, but after this point, when more acid is added, more ferric sulphocyanate is dissolved than is caused to be re-formed by combination of its dissociated ions, and the colour effect decreases. The great effect the free acid has on the stability of the salts is well shown in the case of an equal equivalent solution at 160 litres dilution, where the addition of one equivalent of acid more than doubles the colour effect. The 100 equivalent solution is but slightly affected by the free acid, which forms an additional proof of the greater trustworthiness of the colour constants for such solutions over those obtained with equal equivalent solutions.

Summary.

The chief conclusions arrived at in this paper are the following :—

Solutions of ferric sulphocyanate are greatly influenced by dilution, owing to the salt undergoing dissociation. Solutions containing great excess of ferric salt or sulphocyanate are most stable ; that containing equal equivalents of the salts, the least. On dilution of such a solution from 40 litres to 640 litres, the colour effect is decreased 94 per cent.

The amount of ferric sulphocyanate existing in solutions containing excess of ferric salt decreases on dilution according to the law of mass, but this is not the case with solutions containing excess of sulphocyanate.

On determining the colour reactions of ferric chloride, nitrate, sulphate, tartrate, citrate, and acetate solutions with those of the sulphocyanates of potassium, ammonium, sodium, lithium, calcium, and barium, it was found that the amount of ferric sulphocyanate formed was proportional to the product of two constants : one depending on the nature of the acid of the ferric salt ; the other, on

the nature of the base of the sulphocyanate. The colour constants for the acids show considerable resemblance to their relative affinities, but for the bases there is no resemblance.

Solutions of sulphocyanates and the ferric salts of monobasic acids increase considerably in colour on heating, whilst with the ferric salts of polybasic acids the colour effect decreases considerably on heating.

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Continued from p. 201).

IF Clemente Montemartini's equation $dc/dT = kC$ is correct, there should be two reacting substances, one of constant concentration throughout the reaction. It is, however, to be observed that the values given for the constant k in his results differ widely among themselves, often as much as 25 per cent between the maximum and minimum. Further, all the results in each set of experiments are referred to the first, the C_0 of equation (ii.), though there is no especial reason that this analytical determination should be more exact than those subsequent to it. With the general purport, however, of Martini's paper I cannot but completely agree, namely, that the rate of decomposition of nitrous acid is dependent upon the tension of the superincumbent nitric oxide, without, however, necessarily committing oneself to the view that herein is presented a "true case of dissociation."

It is worthy of remark that the curve representing the decomposition of nitrous acid is exactly identical with that of a previous case of chemical change investigated by myself, namely, the decomposition of formic acid into carbonic oxide and water (*Phil. Trans.*, 1888, A, p. 290), in which the method of observation was precisely the reverse of that adopted in this research. For, herein, the concentration is determined at equal intervals of time,

SERIES XXIV.

Volume of solution = 70 c.c. Temperature, 25.5°.

Ratio of nitrous to nitric acid = 1 : 2.13.

T.	C (observed).	C (calculated). $t = 400$.
		Log $k = 1.250$.
	Grm.	Grm.
0	0.4382	0.4448
30	0.4009	0.4147
60	0.3915	0.3877
90	0.3673	0.3640
120	0.3460	0.3430
150	0.3231	0.3244
180	0.2979	0.3075
210	0.2966	0.2924
240	0.2836	0.2851
270	0.2714	0.2661

SERIES XXV.

Volume of solution = 60 c.c. Temperature, 25.0°.

T.	C (observed).	C (calculated). $t = 170$.
		Log $k = 0.856$.
	Grm.	Grm.
0	0.4157	0.4237
30	0.3646	0.3606
60	0.3190	0.3134
90	0.2881	0.2774
120	0.2484	0.2489
150	0.2381	0.2250
180	0.2102	0.2209
210	0.1894	0.1901
240	0.1647	0.1679

* A Paper read before the Royal Society, June 2, 1892.

SERIES XXVI.

Volume of solution = 70 c.c. Temperature, $24.6^{\circ} \pm 0.1$.
Ratio of nitrous to nitric acid = 1 : 20.7.

T.	C (calculated). $t = 480$. Log $k = 1.452$.	
	Grm.	Grm.
0	0.6707	0.6742
30	0.6262	0.6270
60	0.5789	0.5899
90	0.5537	0.5547
120	0.5255	0.5255
150	0.5065	0.4968
180	0.4775	0.4719

but in the previous case observations were made of the times required for equal diminution of concentration. The results of other series of experiments are given below, the observed and calculated values for the concentration of the nitrous acid being compared in each instance.

In all the above series of experiments the observed and calculated results are as nearly approximate as can be expected, considering the great instability of the nitrous acid, which is appreciably decomposing even in the brief interval of time required for the transference of the solution from the decomposition flask into the potassium permanganate. In the last series of experiments quoted above, in which a considerable proportion of nitric acid was purposely introduced, it is to be noticed that the rate of decomposition is decreased, even though the mass of nitrous acid originally present was greater, which should of course produce an exactly opposite result. This would, therefore, seem to indicate that nitrous acid is more stable in the presence of excess of nitric acid.

Nitrous Acid from Nitric Oxide and Nitric Acid.

Nitric oxide gas was passed into concentrated nitric acid until a deep green liquid was obtained; 10 c.c. of this were then slowly introduced into about five times its bulk of water, and the whole volume finally made up to 100 c.c.

SERIES XXVII.

Volume of solution = 100 c.c. Temperature, $27.7^{\circ} \pm 0.1$.
Ratio of nitrous to nitric acid = 1 : 10.1.

T.	C (calculated). $t = 360$.	
	Grm.	Grm.
0	0.8812	0.8910
30	0.8372	0.8227
60	0.7749	0.7637
90	0.7021	0.6967
120	0.6791	0.6684
150	0.6443	0.6290
180	0.5874	0.5805
210	0.5603	0.5627
240	0.5242	0.5347
270	0.4965	0.5093

The curve representing the course of decomposition of the nitrous acid obtained by this method is precisely identical with that of the nitrous acid from the silver nitrite, though the rate of decomposition is somewhat diminished. For if the series above be compared with Series XXV., which lasted for the same duration of time, yet though the mass undergoing change was nearly twice as great and the temperature 2° higher, both of which conditions would increase the rate, yet there is a difference of only 5 per cent in the amount of nitrous acid which has disappeared in the two cases. This result confirms that of the immediately preceding series in showing the increase of the stability of nitrous acid in the presence of nitric acid.

Another set of experiments was conducted, the condition of temperature being varied,

SERIES XXVIII.

Volume of solution = 100 c.c. Temperature, 11.1° to 11.3° .
Ratio of nitrous to nitric acid = 1 : 10.72.

T.	C (calculated). $t = 860$. Log $k = 1.8811$.	
	Grm.	Grm.
0	0.8910	0.8823
30	0.8716	0.8545
60	0.8467	0.8266
90	0.8046	0.8006
120	0.7815	0.7761
150	0.7595	0.7531
180	0.7337	0.7314
210	0.7033	0.7108
240	0.6759	0.6914
270	0.6710	0.6739
300	0.6454	0.6537

A third set of experiments was also conducted at a higher temperature, other conditions remaining the same.

SERIES XXIX.

Volume of solution = 100 c.c. Temperature, 31.2° .
Ratio of nitrous to nitric acid = 1 : 10.13.

T.	C (calculated). $t = 330$. Log $k = 1.3268$.	
	Grm.	Grm.
0	0.6565	0.6432
30	0.6030	0.5893
60	0.5542	0.5443
90	0.4939	0.4712
150	0.4451	0.4422
180	0.4169	0.4162
210	0.3970	0.3930
240	0.3545	0.3720
270	0.3344	0.3358

On a comparison of the results set forth in the three preceding series of experiments, it appears that the velocity of decomposition of nitrous acid is an exponential function of the temperature, the former increasing in geometrical as the latter increases in arithmetical proportion. This relation may be expressed by the equation—

$$v_t = v_0 k^{(t - t_0)},$$

that is to say, the difference of the logarithms of the amounts of nitrous acid decomposed at the end of a given interval of time will be constant for a constant difference of temperature. This is rendered evident by the following comparison:—

Series.	Temperature.	Percentage loss after 270° .	Logarithms.
(I.)	11.2°	24.00	1.3802
(II.)	27.7	43.01	1.6334
(III.)	31.2	49.09	1.6909

The logarithmic differences for 1° are therefore:—

From (I.) and (III.)	0.0153
" (I.) " (II.)	0.0154
" (II.) " (III.)	0.0167
Mean	0.0158

The rate of chemical decomposition of the nitrous acid is therefore practically doubled for every 20° , which would give a constant logarithmic difference of 0.0151 for every degree. In this respect this change resembles another, otherwise totally different from it, namely, that between marble and hydrochloric acid, which varies by a like amount for equal differences of temperature. This relation is also exemplified by another pair of experiments in which 20 c.c. of nitric acid through which nitric oxide gas had been passed were made with water up to a constant volume of 100 c.c.

SERIES XXX.

Volume of solution = 100 c.c. Temperature, 21.8°. Ratio of nitrous to nitric acid = 1 : 10.2.

T.	C (observed).		C (calculated). $t=400$.	
	Grms.		Const. log = 1.7307.	
0	1.3247		1.3451	
30	1.2522		1.2512	
60	1.1188		1.1175	
90	1.0948		1.0978	
150	0.9992		0.9781	
180	0.9111		0.9275	
210	0.8688		0.8799	
240	0.8254		0.8405	
270	0.7895		0.8010	

SERIES XXXI.

Volume of solution = 100 c.c. Temperature, 31.1°. Ratio of nitrous to nitric acid = 1 : 10.34.

T.	C (observed).	T.	C (observed).
	Grms.		Grms.
0	1.4432	190	0.8219
30	1.2868	220	0.7441
60	1.2045	250	0.6495
90	1.0720	270	0.6045
120	0.9679	300	0.5509

Percentage loss after

270' in series	.. 58.05	Logarithm	1.76385
Do. do.	.. 40.40	"	1.60655
		Logarithmic difference for 1° ..	0.0168

This difference is practically identical with those given above, though the masses of nitric and nitrous acids present were twice as great in the latter than in the former series of experiments.

(To be continued).

THE LAWS AND NATURE OF COHESION.

PART I.

By REGINALD A. FESSENDEN,
Prof. Elect. Engineering, Purdue University, Ind.
(Concluded from p. 207).

The following is a Table of the metals and their Young's moduli. Col. I. contains the observed moduli taken from Sutherland's paper, and Col. II. contains the calculated values from the equation.

Equation III. Young's modulus = $\frac{78 \times 10^{12}}{(\text{atomic volume})^2}$ (corresponding to Equation I.).

Metals.	I.	II.
Iron	2000 $\times 10^9$	1560 $\times 10^9$
Copper	1220	1560
Zinc	930	920
Silver	740	750
Gold	760	750
Aluminium ..	680	690
Cadmium	480	465
Magnesium ..	390	395
Tin	420	295
Lead	190	235

There is only one metal which does not agree with theory, and that is tin (iron, of course, on account of its impurities does not, but we know that, as we obtain iron more pure, we find its rigidity less, so there is very little doubt but that if it were absolutely pure the agreement would be closer). But it is easy to show that the observed results for tin are wrong. For the rigidity is given as

136 $\times 10^9$ and the Young's modulus as 420 $\times 10^9$. Therefore if we represent Young's modulus by $1/a$, then—

$$\frac{a}{2(a+b)} = \frac{136}{420}.$$

Solving this we get $b = 0.55 a$. Therefore the bulk modulus—

$$\frac{1}{3(a-2b)}$$

is negative, and the more tin is compressed the larger it swells, a result which is absurd. This will emphasise the fact that the agreement between theory and experiment is as close as that between the experiments themselves.

It will be noticed that the ratio-rigidity to Young's modulus is about 28/78. Therefore, as $a/2(a+b) = 1/2.7$, Poisson's ratio for these metals is, on the average, 0.35. Therefore the bulk modulus = 1.1 times Young's modulus, which agrees with the only datum I find in Everett, *i.e.*, Wertheim's figures for brass, which gives the ratio 9.48 : 10.2 = 1.08 very closely. All these moduli must contain the atomic volume to the same power, but this is not the case with the tensile strength; for, according to this electrostatic theory of cohesion, we may look at a wire as made up of thin discs, each disc consisting of a layer of atoms. The attractive force between any two such layers would vary inversely as the square of the distance between them and directly as the number of atoms in a layer. Combining these we find that it would vary as the fourth power of the atomic radius, or as (atomic volume)^{2/3}, making no allowance for the effect of temperature on the tensile strength. The following Table gives in Col. I. the observed tensile strengths, taken from Wertheim for wires 1 m.m. in diameter; in Col. II. the atomic volumes of the elements, raised to the 2/3-power; and in Col. III. the calculated tensile strengths as found by the formula.

Equation IV. Tensile strength = $638/(\text{atomic volume})^{2/3}$ in kilograms. for wires 1 m.m. in diameter.

Metal.	I.	II.	III.	IV.
Iron	65	13.7	48	2000 (?)
Copper	41	13.7	48	1327
Platinum ..	35	17.8	36	1800 (?)
Zinc	15.77	19.3	33	690
Silver	29.6	22.2	29	1223
Gold	28.46	22.2	29	1313
Aluminium ..	18	23.2	27	898
Tin	3.40	41	15	504
Lead	2.36	47.8	13	600

Col. IV. contains the melting-points in degrees Centigrade from absolute zero. Here we have to deal with a much more complicated phenomenon than that of rigidity. Rigidity is simply a function of the cohesive force. The tensile strength of a substance depends not only on the cohesive force of the metal, but also on its ability to resist flow. If a metal did not flow before being pulled apart, there is no doubt but that its tensile strength would be proportional to the 2/3-power of the atomic volume. As, however, it does flow, and the amount of flow is not simply proportional to the diminishing of the cohesive force, we have to make a fresh allowance for it. In all the metals the melting-point is reached when the linear expansion has amounted to about 2 per cent. So when the cohesion has diminished about 4 per cent the atoms no longer hold the same relative positions, but one can slip in and take the place of another. So at equal distances from their melting-points only can the tensile strength be proportional to the 2/3-power of the atomic volume. Consequently this ratio can only hold good with substances which have approximately the same melting-point. On examining the Table it will be seen that as copper, gold, and silver have approximately the same melting-point, the ratio does hold good with them. The same with tin and lead. Aluminium and zinc, which should be, the one

slightly weaker, the other slightly stronger, than silver, have a melting-point about one-half that of gold and silver, and they have about half the strength at the temperature of comparison which they should have. The melting-point of iron and platinum is higher than that of gold or silver, and consequently their tensile strength is greater. The flow of a metal depends on two things, the cohesive force and the kinetic energy of the atoms. What function the flow is of the temperature, as reckoned in fractions of the temperature at which the substance melts, it is hardly worth while to go into now. If we suppose it directly proportional (though we may feel fairly certain it is not so simple a function) so that, at the same temperature, a metal melting at half the temperature that another does flows twice as easily, we get the following Table, where Col. I. contains the observed tensile strengths, and Col. II. the calculated ones :—

Metal.	I.	II.
Iron.. .. .	65	74
Copper	41	48
Platinum	35	48
Silver	29.6	29
Gold	28.5	29
Aluminium	18	18
Zinc	15.7	16
Tin	3.4	5
Lead	2.36	4

I have not been able to find any data for the tensile strength of magnesium. Theory gives about 9 kilograms. for a wire 1 m.m. in diameter. It would be interesting to find if experiment confirms this.

If, then, we have met with a new phenomenon in a substance, and are able to show that a certain property already known to exist in the substance is capable of producing effects of the magnitude observed, and that the phenomenon obeys the same laws as it would if it were caused by the already known physical property, we are to a certain extent justified in supposing that this property is really the cause of the phenomenon in question, and in applying our knowledge still further. We have seen that the charges which we know the atoms have on them are able to give effects of the same size as those observed in experiments on tensile strength, and that the various moduli follow the same laws as they would if cohesion were an electrostatic effect, and we may now apply our formula to other and less-known phenomena.

The velocity of sound in a wire is given by the formula :—

$$\text{Velocity} = \left(\frac{\text{Elasticity}}{\text{Density}} \right)^{\frac{1}{2}}.$$

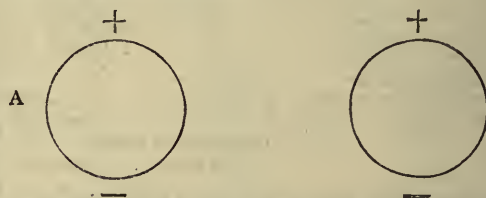
Elasticity here means Young's modulus, the formula for which, as we have seen, was constant $\div$ (atomic volume)², and atomic volume is atomic weight $\div$ density, so we have velocity of sound in wire =

$$= \left(\frac{\text{constant}}{\text{atomic weight} \times \text{atomic volume}} \right)^{\frac{1}{2}},$$

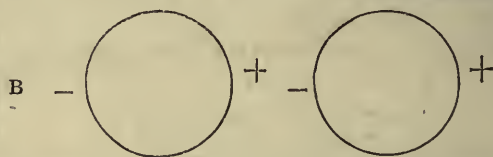
the constant being 78×10^{12} . The following table gives in Col. I. the velocities of sound in wires of a number of metals which have been tested, and in Col. II. the calculated velocities for these and for other metals which have not yet been tested.

	I.	II.	III.
Silver	2.61×10^3	2.7×10^3	100
Copper.. .. .	3.56	4.1	110
Gold	1.74	1.9	136
Alumin.	—	5.1	200
Magnes.	—	4.8	275
Zinc	—	3.6	375
Cadmium	—	2.3	450
Tin	—	2.0	878
Lead	1.23	1.4	1300

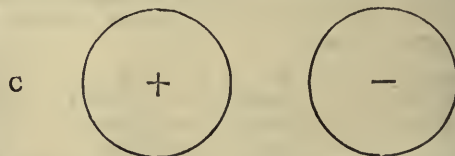
Col. III. gives the electrical resistance, silver being taken as 100, and it may be noticed that in any one group of metals the conductivity varies directly as the velocity of sound, and in passing from one group to another, by multiplying the conductivity by the valency we get proportionate values for all the metals. The same holds good for the heat conductivity. No close agreement can be expected here, for there are too many things to be taken into account. It is merely mentioned here because the fact of their being a relation between the velocity of sound and the conductivity for heat and electricity throws a light on the nature of these phenomena. This will form the subject of a separate paper. It may be asked how an electrostatic force can produce such effects. If the atoms are all similarly charged either + or — they would repel each other and not attract. The explanation is probably this: The atoms, if we may call them so, of electricity are not infinitely smaller than the atoms of matter. When an atom is neutral it does not mean that it has no charge, but that it has equal quantities of both kinds of electricity. The resultant effect of these charges on a body at a distance is zero; it behaves as if it had no charge, as shown below, in A.



If the atoms be brought close together there is a state of unstable equilibrium, and the effect is that either of the charges move on the surface of the atoms or the atoms themselves move so that the atoms attract each other, as in B. Consequently all atoms neutrally charged attract



each other. If nothing further happens, the attraction is simply cohesion. If, however, any third substance connects the two outside parts of the atoms, and so enables these parts to neutralise each other, we have chemical combination, and the two atoms when separated show opposite charges, as in C.



Whether we accept the electrostatic theory of cohesion or not, from the above tables of moduli, the following laws are evident :—

I. In any two metals the force of cohesion varies inversely as the square of the distance between the centres of their atoms.

II. In any one metal the force of cohesion varies inversely as the square of the distance between the centres of its atoms.

We may expect these facts to be of great use in the study of the properties of matter. For, knowing the size and weight of the atoms and the velocity with which they move, all that was wanting to enable us to calculate the behaviour of the atoms of matter, in the same way as we

do the motions of the planets, was a knowledge of the laws of the force which holds them together; and, from the evidence given above, I have no doubt that you will agree with me in saying that we have at least made a beginning in that direction.

A few words might be said about Poisson's ratio. It is, as I said, not fair to argue from the behaviour of cork or indiarubber that there is no relation between longitudinal extension and lateral contraction or between *a* and *b*. When we compress a cork, we are not compressing the substance which forms the cork any more than we are compressing a piece of paper when we crumple it up in our hand. A cork is like a dry sponge, and when we squeeze a sponge up in our hands we are simply doubling up the cell walls, not compressing the substance of the sponge. The only way in which we can determine the compressibility of cork is to soak it in ether or some substance which fills all its pores, and then subject it to hydrostatic pressure. In the same way, when we stretch indiarubber, or ivory, or jelly, the longitudinal extension of the piece of rubber is not in the least a measure of the longitudinal extension of the substance of the rubber. All such substances are made up of two parts; rubber, for instance, of a hard elastic skeleton, insoluble in most solvents, and of a soft plastic substance, soluble in many solvents, by use of which the two parts may easily be separated; similarly, ivory and jelly. Let us take a square cell as in Fig. 3, the walls of which are of elastic material and the contents an incompressible plastic substance. Suppose it to be extended till its length is 4 c.m. and its breadth and thickness each 2 c.m., as in Fig. 4. The total area of cell-wall is 40 square c.m., and the total volume of incompressible contents is 16 c.c. Imagine the cell to be released, it will regain its position as in Fig. 3, and form a cube of side 2.52 c.m. In this case, the volume being the same, the cell area will be 38.1 square c.m. So we find that by stretching the cell till its length was 60 per cent greater than before, we have only had to stretch the cell-walls 5 per cent. This gives us the explanation of the well-known fact that stretched rubber contracts when heated. For if we heat the cell shown in Fig. 4, the incompressible contents will expand and tend to make the cell walls take that shape in which they can hold the most. This is obviously that of the original cube, therefore the result will be a contraction.

Of course the formulæ derived from this theory of cohesion give us the means of calculating the physical properties of metals which have never been examined, or even discovered. For example, it shows us that we have at our disposal a metal far superior to any metal yet known, one which is stronger than iron, lighter than aluminium, and a better electrical conductor than silver. Aluminium, in spite of its lightness, is too weak mechanically, and too poor a conductor to be used in many cases. But this new metal is four times as strong as aluminium, and is twice as good a conductor of electricity. The metal referred to is glucinum or beryllium. All that is known about it is that it has an atomic weight of 9.1 and a density of 1.7 to 2, the exact figures not being known. But from these scanty data we can deduce the following figures:—

Metal.	Rigidity.	Tensile strength.	Conduc'ty.	Sp. gr.
Aluminium ..	250 × 10 ⁹	18 K. grms.	50	2.75
Silver ..	280	27	200	10.5
Iron ..	750	42.65	14	8
Calculated for glucinum ..	1300	65	105	2

We also see why diamond is so hard, and that there is only one other thing that might possibly scratch it, and that is a crystal of manganese. With the exception of glucinum, none of the other metals, either discovered or to be discovered, are likely to be any better than those we have now.

THE USE OF FLUORIDES IN THE MANUFACTURE OF ALCOHOL.*

By Dr. LEO BAEKELAND.

(Concluded from p. 204).

In another series of experiments wort was prepared in the same way, but after being cooled off to 30° C., 3 grms. of yeast per litre were added. This mixture was put in several bottles which were provided with a hydraulic stopper and which could be kept at a temperature of 30°. To the contents of some of these bottles a previous addition of fluoride had been made in quantities equivalent to 6 grms. per hectolitre of wort. After three days fermentation was complete in all the bottles, and the comparative analysis showed:—

	No fluoride.	Fluoride,
		(6 gr. per hectolitre).
Alcohol ..	6.4	7.2
Acidity (normal soda per 100 c.c.) ..	5.6	4.0

The proportion of alcohol in the above results is about 12.5 per cent higher in the sample where fluoride has been used. (See also Effront, "Action des acides mine-raux dans la saccharification par le malt et la fermentation des matières amy-lacées," *Moniteur Scientifique*, 1890; Maerker, "Flussäure verfahren," *loc. cit.*)

The specific action of fluorides on the development and activity of yeast cells has been the object of other interesting experiments. (See Effront, *Moniteur Scientifique*, November, 1891; also Maerker, *loc. cit.*) An addition of small quantities of fluoride, say in 30 m.grms. per 100 c.c., is favourable to the development or increase of the number of yeast cells. Larger quantities (70 to 150 m.grms.) decrease the formation of new yeast cells, and when as much as 250 to 300 m.grms. per 100 c.c. are used, the development of new yeast cells is practically interrupted. But even then, when such large quantities of fluoride are used, the ferment itself is not killed; it has merely suspended the reproductive faculties of the yeast cells, while their alcohol making action is still existent but with lessened activity. Furthermore, if such yeast heated previously with relatively large quantities of fluoride is brought into fresh wort containing no fluoride, it will at once resume its full vital properties, new yeast cells will be produced, and the alcoholic fermentation will be very energetic.

In some experiments small quantities of yeast (0.25 to 0.25 grm. per 500 c.c.) were added to sweet wort made with corn and left to develop with different quantities of fluoride, and afterwards the relative number of yeast cells was determined in each of the samples, with the following results:—

	Acidity	Relative number
	(C.c. normal soda).	of yeast cells.
No fluoride ..	1.10	331
0.02 amm. fluor. ..	0.80	449
0.07 " ..	0.90	381
0.15 " ..	0.70	208

A certain quantity of each of these samples has been added to a fresh wort containing no fluoride (500 c.c. of each sample to 1 kilogr. of wort, 17.4 Sacch.), and after the fermentation was finished the quantity of alcohol produced by the sample was—

	Alcohol.
	Per cent.
No fluoride ..	4.1
0.02 grm. amm. fluor. ..	7.1
0.07 " ..	8.4 (!)
0.15 " ..	8.5 (!)

The above results show clearly that even by starting with a smaller number of yeast cells, more alcohol has been produced, and this is on account of the increased vital powers of these yeast cells after they have been under influence of fluoride.

* From the *Journal of the American Chemical Society*, xiv., No. 7.

The specific action of fluorides is not the same on all varieties of yeast. Four kinds of yeast have been especially examined in this direction:—

Saccharomyces	Cerevisiæ.
"	Pastorianus I.
"	Carlsberg.
"	Bourton.

By addition of 100 m.grms. of fluoride to 100 c.c. of liquid the following results have been observed:—

	Decrease of development of yeast cells by addition of 100 m.grms. fluoride.	Decrease in production of alcohol by addition of 100 m.grms. fluoride.
S. Pastorianus ..	34 per cent	41 per cent
S. Bourton ..	31 "	14 "
S. Carlsberg ..	25 "	13 "
S. Cerevisiæ ..	9 "	4 "

This shows that *S. Pastorianus* is most sensitive to an addition of 100 m.grms. fluoride, the quantity of alcohol decreases to 41 per cent of what can be produced without fluoride. *S. Bourton* and *S. Carlsberg* are less sensitive, but the most resisting of all is *S. Cerevisiæ*. By addition of 300 m.grms. of fluoride the production of new yeast cells is nearly completely stopped in the four varieties, but even then *S. Cerevisiæ* gives about three times as much alcohol as *S. Pastorianus* (see Table).

Name of yeast.	No. of sample.	Fluoride per 100 c.c. m.grms.	No. of yeast cells.	Alcohol, per cent.
Pastorianus I.	1	0	23	7.3
"	2	100	15	4.3
"	3	150	8	2.6
"	4	200	7	2.4
"	5	300	2	1.7
Bourton	6	0	32	7.9
"	7	100	22	6.8
"	8	150	20	5.8
"	9	200	10	4.1
"	10	300	3	4.0
Carlsberg	11	0	16	6.8
"	12	100	12	5.9
"	13	150	10	5.6
"	14	200	6	5.2
"	15	300	2	2.3
Cerevisiæ	16	0	22	7.1
"	17	100	20	6.8
"	18	150	11	5.2
"	19	200	4	4.9
"	20	300	2	4.5

The difference in the resisting power of these four varieties of yeast to the action of fluorides can be used to separate one from another. For instance, if a mixture of equal parts of *S. Pastorianus* and *S. Bourton* (whose cells are easily to be distinguished under the microscope) is kept during 72 hours in a wort containing 300 m.grms. of fluoride per 100 c.c., and afterwards transferred to a wort containing no fluoride, where they are allowed to ferment during 48 hours, and if these operations are repeated three times, it is possible to eliminate entirely all yeast cells of the *Pastorianus* variety.

It is to be noted as an important fact that yeast can be kept for more than six months with an addition of 200 to 300 m.grms. of fluoride per 100 c.c. Even after this time the yeast cells have proved to be in an excellent state of preservation, and when brought afterwards in a wort without fluoride they developed rapidly and produced a splendid fermentation.

The practical results which have been obtained in distilleries, after Effront's process have fully demonstrated

the remarkably useful properties of fluorides. In Europe nearly all important distilleries have adopted the process, and their reports have been very favourable. In general an increase from 8 to 10 per cent in the yield on alcohol has been obtained, and a more steady and more complete fermentation has been noticed. The production of lactic and butyric acid has been reduced to a minimum. The quality of alcohol has also improved, and this is probably due to the prevention of secondary fermentations. The odour and taste of such alcohol is very similar to that of ordinary alcohol that has been filtered over charcoal.

From the beginning when the fluoride process was introduced into distilleries, special experiments have been made in order to see if the presence of small quantities of these salts in the slops or wash did not have unhealthy effect on the cattle using such food. Dr. Tappeiner (*Zeit. des Landwirth's Vereins in Bayern*, 1890) has published some interesting laboratory experiments which show clearly that not the smallest difference has been observed in the use of such slops, either in the composition of the milk nor the general conditions of the animals fed upon it.

Since then practice has entirely confirmed these conclusions. The slops produced from distilleries working with fluoride is far less acid than usual and is remarkable for its keeping qualities. While, usually, slop becomes acid very quickly, it will, on the contrary, keep for weeks without much alteration if fluorides are used. Its taste is sweeter also, and this is probably the reason why in some cases where the fluoride process has been introduced, it took the cattle a few days before being accustomed to this taste. It should be reported, however, that in one case when the slop was used over again in the mashing process the fluorides seemed to accumulate in it, and therefore it is thought advisable not to use the same slop more than twice if it has to be used afterwards for feeding purposes.

CORRESPONDENCE.

A NEW SILVER ORE.

To the Editor of the Chemical News.

SIR,—In reply to Mr. Roger's statement with respect to my note upon a new silver ore, I am perfectly aware of the exhibits he mentions, and of the difference existing between mine and the same. Perhaps Mr. Rogers will read my note again; he will then see that I stated nothing definitely as regards the manufacture of porcelain from the same, which he so pointedly asserts.—I am, &c.,

HENRY N. WARREN.

Uranium.—It is announced that a vein of silver containing a high percentage of uranium has been discovered in South Africa, on a farm belonging to the White Bank Silver Syndicate.

Diagnosis of α - and β -Naphthol.—Herr Verhassel (*Journ. der Pharmacie d'Anvers*) proposes the following reactions:— α -Naphthol in an aqueous solution gives a violet colouration with solution of chloride of lime and of potassium ferrocyanide; with potassium ferricyanide a brown colouration; with ammonia the liquid remains colourless. In an alcoholic solution it gives with ferric chloride a violet precipitate. β -Naphthol in a watery solution gives with chloride of lime a greenish yellow, with potassium ferrocyanide a light yellow, with ferricyanide a greenish yellow, and with ammonia a greenish colouration. In an alcoholic solution it gives a greenish colouration and precipitate with ferric chloride.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 15, October 10, 1892.

On December 7th next the University of Padua celebrates the 300th Anniversary of the day when Galileo entered upon his chair at the University.

Novel Preparation and Photometry of Phosphorescent Zinc Sulphide.—Charles Henry.—According to the author we may obtain in one operation several kilos. of a fine phosphorescent zinc sulphide by treating a perfectly neutral solution of pure zinc chloride with ammonia, re-dissolving the precipitate in an excess of ammonia, precipitating the ammoniacal zinc oxide completely, though without the least excess, with hydrogen sulphide, heating to whiteness with suitable precautions in a crucible of refractory clay placed within a graphite crucible lined with charcoal, washing perfectly the amorphous zinc sulphide and drying it with exclusion of every impurity. Contrary to the alkaline earthy sulphides, zinc sulphide becomes phosphorescent only when perfectly pure. The author finds the mean luminous intensity of this phosphorescent sulphide (5.432 grm. in a tube 10 m.m. in diameter and 42 m.m. in height) = 0.000215 of a normal candle at the distance of 1 metre.

On Pyrogallol Antimonites.—H. Causse and C. Bayard.—The acid antimonite, $C_6H_5O_2 + SbO_3H_3$, forms minute crystals insoluble in water, alcohol, benzene, and chloroform, but soluble in sulphuric, nitric, and hydrochloric acids. The neutral antimonite, $C_6H_5O_3Sb$, differs from the acid compound merely in composition.

On the Tartaric Ethers.—P. Freundler.—The author has obtained the methylic, ethylic, normal propylic, and isobutylic derivatives of the diacetyltartaric, dipropionyltartaric, and dibutyryltartaric (normal butyric acid), as well as the normal butylic ether of diacetyltartaric acid; in all thirteen compounds, all new except the methyl, ethyl, propyl, and isobutyl diacetyltartrates, which have been already studied, but the rotatory power of which have been determined only in solution.

New Method of the Production of Bricks used in Certain Parts of Central Asia.—E. Blanc.—The method in question is used in the western parts of Mongolia, where the extreme and rapid alternations of temperature disaggregate most natural rocks as well as bricks burnt in the ordinary manner. The kiln has the form of a vertical cylinder surmounted by a dome at the top of which is a rather wide hole, which remains open during the first part of the process. Three draught chimneys built inside the furnace open outwards at the height of the dome, and are closed with clay at the beginning of the operation. The fire is kept up for three days, a dry herb, *Alhagi camelorum*, being used as fuel. The third day the hole at the top of the dome is gradually reduced in diameter by means of blocks of moistened clay; the flame is let die down, and the opening is closed with a cover of wet felt forming a kind of bag, which is filled with sand kept constantly wet. The three lateral apertures are unstoppered, and the flame is kept as high as possible for four days. The draught is thus reversed, the steam which fills the interior of the kiln is superheated, and attains a higher pressure than that of the external air. The bricks, which on the third day were of a light red, take a uniform dark grey colour, and become sonorous and very hard, resembling in appearance certain trachytic rocks.

Process for Ascertaining the Purity of Coprah Oil and Palm Oil.—Ernest Milliau.—This paper will be inserted in full.

The Volumetric Determination of Alkaloids.—L. Barthe.—This paper will be inserted in full.

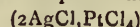
The Part played by Spermine in Intra-Organic Oxidations.—Alex. Poehl.—This paper is rather medical than chemical in its character.

Zeitschrift für Analytische Chemie.
Vol. xxxi., Part 4.

Apparatus for the Development of Gases.—W. Reatz.—The apparatus cannot be intelligibly described without the figure.

A Glass Tripod.—W. Reatz.—A recommendation to make tripods of glass tubing instead of rods.

Action of Barium Peroxide upon Metallic Salts.—W. Kwasnik (*Archiv. der Pharmacie*).—Not merely potassium ferricyanide but a series of other salts act upon barium peroxide so as to liberate oxygen. The salts of the alkalies and alkaline earths do not liberate oxygen, magnesium salts and also those of zinc and cadmium slightly. The salts of nickel, cobalt, iron, manganese, chrome, and aluminium produce a powerful development of gas. The hydroxides of the metals are formed, and half the oxygen of the barium peroxide is liberated. In the salts of the lower oxides of the last group the development of oxygen ensues in two phases. There occurs firstly oxidation, and gaseous oxygen is afterwards liberated. Cupric salts give at once a brisk discharge of gas. Salts of mercury, silver, and gold liberate two atoms of oxygen for each mol. of barium peroxide, and the metallic salts are reduced. Platinum forms an exception to the behaviour of the above-named precious metals. On employing platinum chloride hydrochlorate there is formed a soluble compound resembling potassium-platinum chloride. The double chlorides of platinum and an alkaline earthy metal do not act upon barium peroxide. Platinum chloride ($PtCl_4$) and silver-platinum chloride—



are decomposed with elimination of platinum or platinum and silver. Barium peroxide yields oxygen not merely with soluble metallic compounds, but also with those insoluble in water, though the action is slower.

Determination of the Specific Gravity of Solids.—L. Liebermann (*Math. Naturwissen Berichte aus Ungarn*).—A known quantity of the substance in question is to be precipitated in a vessel of known weight and volume, filled up to the mark with water, weighed, and the specific gravity of the filtrate is determined after filtration. The author recommends pyknometers where the top is ground to fit on not into the recipient.

On Glass and the Influence of its Composition upon its Properties.—A series of papers.

Comparison of Mercurial Thermometers.—Papers by H. F. Wiebe and W. Pomplun (*Zeit. Instrumentenkunde*).—Wiebe's device is not described. Pomplun's apparatus depends on the principle of maintaining temperatures constant by means of a few liquids which are not affected in their composition by prolonged boiling, their points of ebullition being modified by alterations of pressure.

Execution of Reactions at High Temperatures and Pressures.—W. Hempel (*Ber. Deut. Chem. Gesell.*).—The author obtains the heat in the interior of the apparatus by electrical agency, whilst the external walls are kept cool by means of cold water. The arrangement approximates to the electric furnace of W. Siemens.

Characterisation of Flame.—N. Teclu (*Journ. Prakt. Chemie*).—This paper requires the accompanying figure.

A Vacuum Exsiccator capable of being Heated.—J. W. Brühl (*Ber. Deut. Chem. Gesell.*).—A transportable air-pump plate contains beside the middle aperture, which serves for evacuation, two lateral perforations

through which tubes from the source of heat are introduced.

Development of Gases.—C. G. Moor.—From the CHEMICAL NEWS.

New Weighing-Bottle.—C. Mangold.—This note requires the accompanying figure.

New Apparatus for the Extraction of Fats.—J. T. Willard and G. H. Failger (*Journ. Anal. App. Chem.*).

Pipette for Mercury.—V. Dvorak (*Zeit. fur Instrumentenkunde*).—Both these papers require the appended illustrations.

New Method for Producing Hydrobromic Acid.—G. S. Newth.—From the CHEMICAL NEWS.

New Methods of Quantitative Analysis.—A. Baumann.—This memoir is in the course of insertion.

Detection of Salicylic Acid in Salicylaldehyde and in Salicylic Methyl ester.—A. Schneegans and J. E. Gerock (*Journ. d. Pharm. von Elsass-Lothringen*).—Already inserted.

Reagent for Guanidines.—O. Prelinger (*Monatshefte fur Chemie*).— α -Triphenylguanidine picrate is very sparingly soluble in cold water. Aqueous solutions of α -triphenylguanidine are at once precipitated by picric acid. Since phenylguanidine and methylguanidine behave in a similar manner with picric acid, the author considers that it may be considered a general reagent for the guanidines.

Ultimate Analysis of Nitrogenous Substances.—Clemens Gehrenbeck and Felix Klingemann have made communications on this subject in the *Ber. Deut. Chem. Gesell.*

Oxidation of Organic Compounds by Potassium Permanganate.—R. Benedikt and J. Neundörfer (*Chem. Zeit.*), and C. Micko (*Zeit. Oesterr. Apoth. Vereins*).—The two former authors studied the conditions under which ethyl alcohol is converted into oxalic acid by permanganate, but without success. Micko endeavoured to determine malic acid by complete oxidation with permanganate, but he did not arrive at any satisfactory results.

Separation of Malic Acid from the Succinic, Citric, and Tartaric Acids.—C. Micko (*Zeit. des Oesterr. Apoth. Vereins*).—This paper will be inserted in full.

Determinations of Tannin.—A. Klinger and A. Bujard (*Zeit. fur Angew. Chemie*) come to the same conclusion concerning the Gantler process as do Von Schröder and Passler. The consumption of permanganate by tanniferous solutions after the tannin has been precipitated by hide-powder must by no means be neglected. If this point is overlooked, an error of 5 per cent in excess is obtained in case of oak bark. As the hide-power generally contains soluble organic substances, their consumption of permanganate must be ascertained and deducted.

Determination of Glycerin in Wine.—Th. Lecco (*Chem. Zeit.*).—This paper will be inserted in full.

Balance for Determining Percentage Changes in Weight during Evaporating, Drying, Roasting, &c.—G. W. Barth (*Zeit. Angew. Chemie*).—This apparatus consists of a beam resting on a pillar. One half of the beam is divided into 100°, and on it is a movable capsule-shaped counterpoise. To the other arm of the beam there is attached a scale pan for receiving the substance in question. The weight of the scale pan is compensated by means of a weight fixed to the graduated arm; the counterpoise is moved to 100°, and the substance to be examined is placed in the scale pan. The capsule-shaped counterpoise is loaded with shot, and the balance allowed to play. The scale pan with the substance in question is now exposed to the desired agency, generally heat. If there occurs a loss of weight, equilibrium is restored by displacing the capsule-shaped counterpoise, and the percentage of the substance which has not been volatilised can be read off from its position.

A Calorimeter.—H. Pellet and A. Demichel (*Bull. de l'Assoc. Belge des Chimistes*).—The apparatus consists of two long horizontal tubes laid side by side, one of them serving to receive the paler comparative solution. To the other tube is fixed a relatively large funnel, by means of which 10 or 20 c.c. of the darker solution may be introduced. By adding measured quantities of water and mixing by forcing air into it, the darker solution is diluted until the colour in both is equal in shade.

Bulletin de la Société Chimique de Paris.
Series-3, Vols. vii. and viii., No. 14.

Preparation of Basic Zinc Acetate in Crystalline Needles.—A. Terreil.—The author obtains this substance by the prolonged action of dilute nitric acid. The compound obtained corresponds to the formula $5(\text{ZnO})\text{NO}_3 \cdot 5(\text{HO})$.

Residues from the Preparation of Propylenic Glycol.—L. Raisonier.—The action of soda upon glycerin at elevated temperatures yields propylenic glycol mixed with a certain quantity of alcohols. From this mixture the author has separated ethylic and allylic alcohols. Methyl alcohol may be considered as the chief product of the reaction. Propylic alcohol was not obtained.

MEETINGS FOR THE WEEK.

WEDNESDAY, NOV. 2nd.—Society of Public Analysts, 8. (1) "Note on a Sample of Poor, but undoubtedly Genuine Milk," by C. W. Heaton. (2) "Composition of an Abnormal Sample of Milk," by Alfred Smetham. (3) "Note on a case of Abnormal Milk," by Dr. Bernard Dyer.

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THE CHEMICAL NEWS.

VOL. LXVI, No. 1719.

PRELIMINARY NOTE ON THE ACTION OF DRY AMMONIA-GAS ON SULPHATES.*

By W. R. HODGKINSON and C. C. TRENCH, Col. R.A.

VERY little appears in chemical literature as to the action of really dry ammonia-gas on salts at an elevated temperature. Some chlorides are said to be reduced, others to yield nitrogen compounds when heated with ammonia, but little or nothing seems to be known respecting the action with sulphates.

The experiments were undertaken to ascertain (1) to what extent, if any, sulphates were reduced by ammonia at temperatures below that at which the sulphate itself decomposes; and (2) whether nitrogen compounds (nitrides) could be formed.

All the work has been quantitative as far as possible. After a number of preliminary experiments the reactions were carried on in a wide glass tube so arranged that it could be heated in an air-bath to a definite temperature when required or by the naked flame. The substance was contained in a boat of platinum or porcelain as the case demanded, which with its contents was weighed before and after the action. The ammonia was dried by passing first over potassic hydrate, and then over a considerable quantity of freshly ignited lime.

As water is, however, certainly one product of the mutual action of ammonia and sulphates, this drying is perhaps not an essential precaution. To catch volatile products the tube was drawn out to about 50 c.m., and either dipped into water or ended in a dry flask externally cooled.

General Results.

The preliminary experiments showed that some metallic sulphates were entirely reduced by heating with ammonia. Silver, mercury, and bismuth behaved in this manner. Water, and what at first appeared to be ammonium sulphite, were the only products of a volatile nature. The actions were completed at the melting-point of zinc.

Lead sulphate required a high temperature before any action was visible, and the salt was not completely decomposed by heating for an hour at a red heat. A little lead sulphide was produced. Thallium sulphate acted in a similar manner, but more sulphide was formed.

Ferrous sulphate (dry) precipitated by addition of strong acid to the concentrated water solution of FeSO_4 , and then dried *in vacuo*, ordinary crystallised ferrous sulphate, and the ammonium ferrous sulphate were all reduced to metallic iron, which, however, contained 1 to 2 per cent of sulphur. The sulphates of zinc, magnesium, cobalt, nickel, manganese, and chromium were remarkably alike in their behaviour.

In all these cases the quantity of material left in the boat after heating corresponded very closely with that required if a sulphide of the form MS_2 had been formed. As a matter of fact, the residue consisted of a mixture of the sulphide and oxide in nearly molecular proportions. No nitride has as yet been obtained.

As far as the volatile portion is concerned, the main bulk in all cases appeared at first to be ammonium sulphite. No trace of sulphate was found. In the hot tube in which the reaction was carried on, the substance which condensed was for the most part ammonium thionamate, $\text{NH}_3\text{OHSONH}_2$. Where this came in contact with water

in the condensing flask or with moisture in the cooler parts of the tube, ammonium sulphite was of course formed.

Undoubtedly the most interesting salt examined is cupric sulphate. Either dry or with crystal water, the salt absorbed much NH_3 , and then melted below 200° , turned black, and as the temperature rose appeared to boil, and finally at somewhere about 400° began to decompose with incandescence, leaving almost pure metallic copper.

The comparatively low temperature at which an action was observable in the case of copper sulphate suggested the possible formation of a hydrazin compound.

The white sublimate was therefore examined for its reducing power on Fehling's solution and silver nitrate. As thionamate reduces both silver and copper solutions when alkaline, some of the white sublimate was distilled from potassium hydrate solution and the distillate collected in dilute sulphuric acid. This solution also reduced Fehling's solution. There is little doubt but that hydrazin is present along with the thionamate sublimate, but the quantity is small, and in several experiments could not be detected at all, probably on account of the temperature being too high when the ammonia comes in contact with the sulphate.

We are continuing this work in the hope of getting an easy method for the production of hydrazin compounds.

ON THE VOLUMETRIC DETERMINATION OF THE ALKALOIDS.

By L. BARTHE.

I HAVE ascertained that the best known alkaloids of vegetable origin are without action upon phenolphthalein, which they leave in the state in which it comes into contact with them; colourless if the medium is neutral or acid, rose coloured if it has been rendered alkaline by a mineral base. Such are quinine, cinchonine, cinchonamine, cinchonidine, quiniidine, morphine, codeine, cocaine, aconitine (amorphous or crystalline), strychnine, brucine, serine, veratrine, pilocarpine, duboisine, spartein. On combining this observation (made, I believe, for the first time) with the well-known property of the vegetable bases to turn red litmus blue, I have founded a general method for the volumetric analysis of the alkaloids.

If certain vegetable principles, hitherto regarded as alkaloids, do not react appreciably with phenolphthalein and litmus, it is doubtless because their properties are still imperfectly known, and that their chemical functions require accurate determination. For instance, narcotine, which, according to Piçet and Flückiger, can scarcely be regarded as an alkaloid and which is without action upon phenolphthaleine, litmus, and atropine, which with these substances behaves like a weak acid.

However it may be, the alkaloid to be determined must be brought to the condition of a soluble salt by means of a mineral acid, *e.g.*, sulphuric acid, either in water or in a slightly alcoholic solution. An excess of acid does not prevent the reaction, but on the contrary rather promotes it. The presence of any salt of the alkaline or earthy bases, and even of a certain number of the heavy metals (*e.g.*, zinc), has no effect upon the process.

The following method of operation is very easily applicable to the determination of the alkaloids above mentioned, and also of the acids with which they may be combined.

Determination of the Acid.

We introduce into a beaker of Bohemian glass 1-1000 part of an equivalent of the alkaloid or of a salt of the alkaloid, adding 10 c.c. of decinormal sulphuric acid in case of a salt, or 20 c.c. in case of a free alkaloid. We add 20 c.c. of neutral alcohol at 90 per cent, and three or four drops of an alcoholic solution of phenolphthalein.

* Read before the British Association, Edinburgh Meeting, 1892.

All the salts of the alkaloids dissolve in this acid alcoholic liquid. We then pour in decinormal potassa until there appears a faint rose-coloured tint of phenolphthalein. The number of c.c. of decinormal potassa used expresses all the acid, free or combined, existing in the mixture. The rose-tint of phenolphthalein appears only when all the alkaloid is in the free state in the liquid; as a transparent solution if the alkaloid is soluble in weak, neutral alcohol, or as a precipitate if it is insoluble. We have thus a mixture indifferent to phenolphthalein, but alkaline to litmus in consequence of the liberation of the alkaloid.

Determination of the Alkaloid.

Into a second beaker of Bohemian glass we introduce 1-1000 of an equivalent of the alkaloid, or of a salt of an alkaloid, with 10 or 20 c.c. of decinormal sulphuric acid, and then some drops of a sensitive tincture of litmus. The colour is then rendered blue again by means of decinormal potassa. The number of c.c. of the alkaline liquid employed in this second saturation represents merely the free acid. If this number is subtracted from the figure which in the foregoing operation measures the entire acid, it expresses exactly the quantity of sulphuric acid combined with the alkaloid in the state of a basic salt, and consequently the weight of the alkaloid itself. It is, in fact, sufficient to multiply the remainder from the subtraction by 1-10000 of the equivalent of the alkaloid in question. The factors are evidently:—

For anhydrous quinone	0.0324
„ cinchonine	0.0294
„ codeine (H ₂ O)	0.0317
„ morphine (H ₂ O)	0.0303

—*Comptes Rendus*, vol. cxv., p. 512.

PURITY OF THE OIL OF COPRAH AND OF PALM-OIL.

By ERNEST MILLIAU.

At from 30° to 31° the oil of coprah, if pure, is soluble in twice its volume of absolute alcohol. At the same temperature palm oil is soluble in four times its volume of absolute alcohol. If mixed with sparingly soluble vegetable oils or animal fats to the extent of 1-20th, or less, both become almost insoluble in the same quantity of absolute alcohol, the solvent action of which does not occasion a fractionated separation of the component parts. The mixture has acquired a solubility which is peculiar to it, and which does not depend on the proportions of soluble and insoluble fatty matters of which it is composed.

These differences of composition enable us to determine with precision the purity of these solid oils, a chemical analysis of which often gives uncertain and even contradictory results, especially for slight admixtures.

Method of Operation.

First Process.—We shake up for one minute, in a test-tube graduated in c.c., 20 c.c. of the oil under examination with 40 c.c. of alcohol at 90°. This indispensable preliminary treatment may give certain indications. Alcohol at 95° absorbs a certain quantity of the neutral fatty substances, and the oil itself dissolves from 15 to 20 per cent of alcohol. The solvent power of the oil decreases appreciably on the addition of insoluble oils, whilst that of alcohol increases by the addition of oils soluble in alcohol at 95°, such as castor and resin oils,—oils which may then be easily characterised by their very distinct chemical and physical properties.

Second Process.—In a test-tube graduated in c.c. we treat 5 c.c. of the oil of coprah (previously washed with alcohol at 95°) with 10 c.c. of absolute alcohol, and we place the tube in a water-bath heated very exactly to from

30° to 31°. After some moments the tube is taken out, shaken very briskly for thirty seconds and returned to the water-bath. Pure coprah oil dissolves entirely, and the alcoholic solution is perfectly clear.

Coprah oil mixed with insoluble oils (the commonest sophistication), arachis, sesame, cotton, maize, &c., does not dissolve appreciably, and forms a turbid mass with the absolute alcohol, from which it quickly falls in fine drops to the bottom of the tube, where it collects. Oil of coprah containing palm-oil is precipitated when the proportion of the mixture reaches 20 per cent. Below that limit the mixture remains turbid.

The verification of palm-oil is effected in the same manner, using 20 c.c. of absolute alcohol instead of 10 c.c., and operating always upon 5 c.c. of oil at the temperature of 30° to 31°.

Five c.c. of palm-oil containing 20 per cent of coprah or upwards dissolves in 15 c.c. of absolute alcohol; in the same proportions the pure oil does not completely dissolve and the mixture remains turbid. The purity of coprah and palm oil cakes is found by extracting a sufficient quantity of oil by means of any solvent and treating in the same manner.—*Comptes Rendus*, vol. cxv., p. 517.

QUANTITATIVE DETERMINATION OF LEAD.

By LUDWIG MEDICUS.

IN operating upon galenas the author adopts the following method:—After converting the lead into a chloride he dissolves the lead chloride in potassa-lye, and passes a current of carbonic acid through the solution for two hours. The precipitated carbonate is filtered off, washed, dissolved in nitric acid, and the lead is precipitated electrolytically as peroxide.

He attempted also to precipitate the lead from the alkaline solution as peroxide by means of bromine. He succeeded best in the following manner:—The chloride is dissolved in potassa-lye; the solution is poured into a flask closed by a cork, with two perforations for the introduction and the escape of gas. A slow current of gaseous bromine is passed through the entrance tube above the liquid, which is gently heated. The bromine is readily absorbed and the lead is gradually deposited as peroxide. The filtration is best effected by exhaustion through finely elutriated asbestos placed between two discs of asbestos paper.—*Ber. Deutsch. Chem. Gesell.*, vol. xiv., p. 2490.

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 213).

Determination of Combined Iodine and Iodic Acid.

WITH the possibility of determining free iodine accurately in a gas-volumetric manner, it becomes possible to effect a determination of combined iodine in iodides and iodates. It is easy to eliminate iodine from its combinations in a free state.

For determining iodine in iodides we distil the sample with acid ferric sulphate, receive the liberated iodine in a solution of potassium iodide, and shake up the distillate with alkaline hydrogen peroxide in the manner above described. It is preferable to make up the distillate to a known volume (100 c.c.), and effect the determination in a part (50 c.c.), so that a check analysis can be effected with the rest.

In order to determine iodic acid we add to the liquid

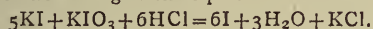
* *Zeit. für Angew. Chemie und Zeit. für Analytische Chemie.*

containing the iodate potassium iodide, and then a slight excess of sulphuric or hydrochloric acid, and determine the liberated iodine according to the gas-volumetric method.

Like iodic acid, other substances which liberate iodine from potassium iodide, without the use of sodium thiosulphate, may be determined much more simply and quickly gas-volumetrically than by titration. Baumann, in conjunction with Kestler, is still engaged with experiments in this direction.

Determination of Free Acids—Acidimetry without Normal Alkali.

F. Mohr expressed the opinion that free acid might be determined by means of potassium iodide and potassium iodate, since even weak acids liberate iodic acid, which, then in contact with potassium iodide, sets free iodine. For each atom of hydrogen in the acid an atom of iodine is liberated according to the equation—



The free iodine is then determined in the usual manner.

This method, which was not able to establish itself, was again brought into notice by Kjeldahl, when he made known his new method for the determination of nitrogen in organic substances. In a subsequent communication he returned to his proposal and recommended to render the solution of sodium thiosulphate more permanent by dissolving the salt in water which has been recently boiled and preserving the solution from light and from carbonic acid. The thiosulphate solution is conveniently adjusted to a solution of iodine of known strength, or, as proposed by Knublauch, we prepare a solution of pure ammonium sulphate (1 grm. in 100 c.c.), and subject 10 c.c. of this solution to distillation with potassa-lye, having a known quantity of acid in the receiver. The standard of the thiosulphate solution is found in the latter case by difference if we take a quantity of acid equal to that used in the distillation, and mix the distillate with potassium iodide and potassium iodate, and in both cases determine the liberated iodine with the solution of thiosulphate.

Standardising the solution of thiosulphate for normal acid directly by determining the iodine liberated by the latter in a solution of potassium iodide and potassium iodate yields no absolutely accurate values, since in dilute acids the reaction only proceeds gradually. The same quantity of iodine which in dilute solutions separates only after some time, depends on the dilution of the liquid and increases on further dilution. It is hence to be recommended to use in titration always an equal volume of liquid, although the fault occasioned by this retarded separation of iodine is always very trifling.

In determining ammonia by distillation Kjeldahl recommends the excess of normal acid to be titrated back in the following manner.

After completing the distillation the distillate is diluted with water to 100 c.c., since, according to what has been said, the volume of the liquid is important, and there are then added 10 c.c. of a 5 per cent solution of potassium iodide, starch paste, and 2 c.c. of a four per cent solution of potassium iodate.

For preparing the starch paste Kjeldahl digests potato starch for a week at the common temperature with dilute hydrochloric acid, washes by decantation, and dries between filter-paper. Starch thus treated, if heated, yields a solution which keeps unchanged if saturated with sodium chloride.

On the determination of acids and bases, especially ammonia, by means of iodine and thiosulphate, E. Pfüger has communicated an elaborate investigation. Pfüger determines the effective value of the thiosulphate solution by mixing 10 c.c. of sulphuric acid, 1 c.c. of which corresponds to 0.001 grm. of nitrogen with 1 c.c. of a 20 per cent solution of potassium iodide, and 1.3 per cent of a 4 per cent solution of potassium iodate. The thio-

sulphate solution is then added until the colour produced by the free iodine has disappeared. Pfüger rejects the use of starch paste in titrations, as it exerts a disturbing influence on the result. If a very dilute solution of iodine is coloured faintly blue with a small quantity of dilute starch paste, and is then mixed with more starch paste, the colour of the liquid often disappears. Pfüger ascribes this phenomenon to the fact that nearly all commercial starch contains a nitrogenous body, probably albumen, which eliminates the iodine from the starch iodide.

(To be continued).

THE CONDITIONS OF THE FORMATION AND DECOMPOSITION OF NITROUS ACID.*

By V. H. VELEY, M.A.

(Concluded from p. 217).

Nitrous Acid from Nitrogen Peroxide and Water.

ABOUT 1 to 2 c.c. of nitrogen peroxide were slowly added to 50 c.c. of water, the liquid being kept continually stirred; after the mixture had become uniform the volume was made up to 100 c.c. as before. By this means a dilute solution of nitrous and nitric acids was obtained. The method of experiment was conducted as usual.

SERIES XXXII.

Temperature, 21.8°. Nitrous acid present after complete admixture = 1.0663 grms. Nitric acid present after complete admixture = 2.3544 grms. Ratio of nitrous to nitric acid = 1 : 2.12.

T.	C (observed). Grm.	C (calculated). Const. log = 1.9819. Grm.
		Grm.
0	0.9181	0.9292
30	0.951	0.9049
60	0.8952	0.8801
90	0.8597	0.8560
120	0.8373	0.8341
150	0.8171	0.8129
180	0.7819	0.7927
210	0.7618	0.7718
240	0.7538	0.7553
270	0.7381	0.7380

The Table below contains the results of another set of experiments with a more dilute solution.

SERIES XXXIII.

Temperature, 21.8°. Nitrous acid = 0.7292 grm. Nitric acid = 1.5457 grms. Ratio = 1 : 2.02.

T	C (observed). Grm.	C (calculated). Const. log = 1.5587. Grm.
		Grm.
0	0.7292	0.7247
30	0.6811	0.6830
60	0.6401	0.6464
90	0.6166	0.6279
120	0.5843	0.5840
150	0.5570	0.5543
210	0.5095	0.5080
240	0.4856	0.4892
270	0.4736	0.4702
300	0.4502	0.4525

The greatest difference between the observed and calculated results is shown in the first two experiments, but this can in part be accounted for by the difficulty experienced in introducing the nitrous acid solution into the permanganate before that some of the liquid was projected from the measuring vessel by the rapidly evolved nitric oxide gas. The above three series of experiments show

* A Paper read before the Royal Society, June 2, 1892.

SERIES XXXIV.

Temperature, 31.8°. Nitrous acid = 2.4557. Nitric acid = 2.2571. Ratio of nitrous to nitric acid = 1 : 0.93.

T.	C (observed).	C (calculated). $t=160$.
	Grms.	Grms.
0	2.2321	2.3180
30	1.9764	1.9077
60	1.6981	1.6858
90	1.4778	1.4833
165	1.1924	1.1413
180	1.1081	1.0937
210	0.9986	1.0024
240	0.9010	0.9271

that whether the nitrous acid produced from nitrogen peroxide and water is of a concentration of 0.45 per cent, or five times that amount, the rate of decomposition is in accordance with the mathematical formulæ given, since, as it happened by chance, the Series XXXII. to XXXIV. were continuous as regards the masses of nitrous acid contained therein.

Nitrous Acid from Nitrous Fumes and Water.

When nitrous fumes from arsenious oxide and nitric acid are passed into water at ordinary temperatures of 12 to 15°, their absorption is apparently very incomplete; a liquid is obtained nearly colourless, and containing 1 to 2 per cent of free nitrous acid. This solution gives off bubbles of gas very freely, especially when poured from one vessel to another, thus recalling to mind the behaviour of solutions of hydrogen peroxide. This very rapid evolution of gas introduced, as explained above, unavoidable errors in the method of experiment adopted; there is therefore not so complete an accordance between the observed and calculated values as in the other series of experiments.

SERIES XXXV.

Temperature, 31.7°. Nitrous acid = 0.7685 gram. Nitric acid = 0.6753 gram. Ratio of nitrous to nitric acid = 1 : 0.88.

T.	C (observed).	C (calculated). $t=160$.
	Grm.	Grm.
0	0.7685	0.7697
60	0.5665	0.5628
90	0.4828	0.4953
170	0.3898	0.3752
200	0.3501	0.3439
230	0.3342	0.3174
260	0.2963	0.2948

The rate of decomposition is nearly identical with that of Series XXXIV., conducted at the same temperature, and in which the ratio of nitrous to nitric acid was also nearly identical.

SERIES XXXVI.

Temperature, 19.8°. Nitrous acid = 1.1789 grms. Nitric acid = 0.3973 gram. Ratio of nitrous to nitric acid = 1 : 0.34.

T.	C (observed).	C (calculated). $t=160$.
	Grms.	Grms.
0	1.1789	1.200
30	0.9680	1.0008
60	0.8453	0.8589
90	0.7853	0.7513
120	0.7109	0.6674
180	0.5444	0.5440
210	0.5022	0.5022
240	0.4703	0.4624
270	0.4317	0.4294
300	0.4063	0.4008

It follows, therefore, from the experiments, the details of which are given above, that solutions containing both nitrous and nitric acids, whether prepared from silver

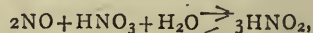
nitrite and hydrochloric acid, or from nitric oxide and nitric acid, or from nitrogen peroxide and water, or from nitrous fumes and water, have this one property in common, that the diminution of reducing material, presumably nitrous acid, therein contained, proceeds in accordance with the same law. The velocity of the change seems, however, to be dependent rather upon the ratio of nitrous to nitric acid than upon the actual masses of either of them. But though these solutions have this one point in common, yet in other respects they differ most markedly. For bubbles of gas, namely, nitric oxide, are rapidly given off from solutions prepared from nitrogen peroxide and nitrous fumes, and to a less degree from silver nitrite, though solutions from nitric oxide and nitric acid do not give off bubbles of gas in a similar manner. Again, all my former investigations (*Journ. Soc. Chem. Industry*, 1891, p. 1294) have shown that, whereas metallic lead does not readily dissolve in solutions containing nitrous acid and prepared from silver nitrite, yet it dissolves very rapidly in solutions equally containing nitrous acid, but prepared from nitrogen peroxide and water. The cause for the similarity on the one hand, and the dissimilarity on the other, must remain the subject of a fuller enquiry.

General Conclusions.

The main points of this enquiry may briefly be summarised as follows:—

(i.) The formation of the impurity of nitrogen peroxide in nitric acid, imparting to it the well-known yellow tint, takes place in the case of the more concentrated acid, even at a temperature of 30°, and of the less concentrated acids at from 100—150°, even when the acid is not unduly exposed to sunlight.

(ii.) The reaction between nitric oxide and nitric acid may be regarded as reversible, thus—



provided that the acid be sufficiently dilute, and the temperature sufficiently low. Under these conditions equilibrium is established between the masses of nitric acids when the ratio of the former to the latter is, roughly speaking, as 9 : 1. The actual ratio varies slightly on the one side or the other, according to the conditions of the experiments. With more concentrated acids and at higher temperatures the chemical changes taking place are more complicated and the decomposition of the acid more profound.

(iii.) The decomposition of solutions containing both nitric and nitrous acids is also investigated; the rate of the change is shown to be proportional to the mass of the nitrous acid undergoing change. The curve representing the amount of chemical decomposition in terms of the mass present is shown to be hyperbolic and illustrative of the law—

$$(I.) \frac{dC}{dT} = -\frac{C^2}{M}.$$

This holds good, whatever be the method employed for the production of the nitrous-nitric acid solution.

The observed values for C or the concentration of the nitrous acid are concordant with those calculated according to the above differential equation within the limits of experimental error.

The rate is dependent upon the ratio of the masses of the nitrous and nitric acid, being the more rapid the greater the proportion of the former to that of the latter.

In the particular case of the liquid prepared from nitric oxide and nitric acid, wherein the reproduction of solutions of similar concentration presents less difficulty, it is shown that, as the temperature increases in arithmetical the rate of change increases in geometrical proportion, in accordance with the equation—

$$(II.) v_t = v_1, k^{(t-t_1)},$$

the value for k being 0.0158.

Finally, though the nitrous-nitric acid solutions behave in a similar manner as regards the diminution of the mass of the nitrous acid, yet, in other respects, such as evolution of gases and the action upon metals, they are dissimilar.

In conclusion I would express my obligations to Mr. W. Eason for assistance in the mathematical portion of the paper, and to my colleagues for suggestions made in the course of the investigations.

ON THE GUNNING-KJELDAHL METHOD AND A MODIFICATION APPLICABLE IN THE PRESENCE OF NITRATES.*

By A. L. WINTON, Jun.

The Gunning Method (in Absence of Nitrates).

THE modification of the Kjeldahl method, proposed by Gunning in 1889, has since been indorsed by a number of well-known chemists.

The Gunning method is very simple, the only reagents used previous to the distillation with caustic soda being sulphuric acid and potassium sulphate, the latter taking the place of the three reagents—mercury (oxide or metallic), potassium permanganate, and potassium sulphide—ordinarily used.

The mixture of sulphuric acid and potassium sulphate boils at a high temperature, and, as a rule, oxidises the organic substance more rapidly than the ordinary mixture of sulphuric acid and oxide of mercury.

The results obtained by Gunning (*Fres. Zeit.*, xxviii, 188), Atterberg (*Chem. Zeitung*, xiv, 509), Van Slyke (*U.S. Dept. Agr. Div. Chem. Bull.*, xxxi, 142), and others, including the writer, on fodders, dairy products, fertilisers free from nitrates, and various organic substances, show that this method is fully as accurate as the ordinary Kjeldahl method, and, in some cases, gives better results. It is a well-known fact that the nitrogen of many alkaloids, azo-compounds, and various bodies of the aromatic series cannot be determined by the usual Kjeldahl method, but Gunning and Atterberg have obtained good results on morphine, quinine, indigo, and aniline oxalate by the Gunning modification.

The chief disadvantage of the method is the frothing which occurs during the first part of the heating. This frothing, however, causes but little trouble if a flask of at least 500 c.c. capacity (which can afterwards be used for the distillation) is employed and care be taken in adjusting the heat.

The Gunning mixture is, at ordinary temperatures, half solid, and must be heated before it can be measured for use. It is therefore best to add 18 grms. of potassium sulphate and 20 c.c. of sulphuric acid, separately and in the order named, to the flask containing the substance, shaking a few times before heating. The coarsely powdered sulphate may be conveniently measured out in a cartridge shell adjusted to hold 18 grms. and provided with a wire handle. The acid may be added from a graduated cylinder or a burette of wide calibre connected by a syphon with the acid reservoir ("Report Conn. Agl. Expt. Station," 1889, 192).

After the digestion is completed water should be added before the mixture becomes too cold, otherwise it is difficult to obtain a solution of the solid mass.

The writer has found that the fertiliser-chemical known in the trade as "high grade sulphate of potash," and costing but a few cents a pound, answers every purpose, and is, in fact, better than the white sulphate of the apothecary, being usually free from moisture and chlorides, the presence of which tends to increase the frothing.

Following is a comparison of results, obtained by the methods named, on those forms of organic nitrogenous matter which are most commonly used in mixed fertilisers and on four commercial fertilisers free from nitrates.

	Kjeldahl method.	Gunning-Kjeldahl method.
Cotton-seed meal	7.06	7.11
" "	7.10	7.13
" "	7.10	7.15
" "	6.95	6.97
Castor pomace	5.56	5.59
Tankage	5.03	5.07
" "	5.72	5.82
Bone	4.03	4.02
" "	3.92	3.90
Dry ground fish	8.69	8.77
" "	8.14	8.06
Peruvian guano	2.88	2.95
Mixed fertiliser*	3.45	3.45
" " †	3.00	3.00
" " ‡	3.80	3.76
" "	1.82	1.81

The Modified Method Applicable in the Presence of Nitrates.

In laboratories where fertiliser analyses are being made the adoption of the Gunning method would tend to complicate rather than to simplify matters so long as in the presence of nitrates nitrogen is determined by another method.

It is impracticable to add salicylic acid to Gunning's reagent, as such a mixture could only be used while hot, and it is important that the temperature be kept as low as possible during the early stages of the digestion. It occurred to the writer, however, that Scovell's mixture of sulphuric and salicylic acids might be used in the ordinary way, potassium sulphate being added later in the process in place of mercury. After a number of unsuccessful trials—unsuccessful because too much potassium sulphate was used and the boiling-point of the liquid became so high that oxides of nitrogen were driven off—the following plan was settled upon:—

The material, 0.5 to 1.0 grm., is digested with 80 c.c. of Scovell's salicylic acid mixture (30 c.c. of sulphuric acid and 2 grms. salicylic acid) in a flask of 600 c.c. capacity for two hours with frequent shaking. Two grms. of zinc dust are then slowly added, with continual shaking, and the flask heated, at first gently, until after a few minutes' boiling dense fumes are no longer given off. Thus far the process is the same as in the Scovell-Kjeldahl method (the official method of the Association of Official Agricultural Chemists), except that the digestion is continued for two hours, which, in some cases, the writer has found absolutely necessary in order to secure complete solution of the nitrate. Ten to twelve grms. of potassium sulphate are next added and the boiling continued for a little time after the solution is colourless or, if iron is present, has a light straw colour which remains unchanged. On cooling, as the mixture begins to solidify, water is added, at first slowly with shaking, and the distillation with caustic soda is carried on in the usual manner.

The trials thus far made with this method on nitrates and fertilisers containing nitrates have proved entirely satisfactory.

In the following Table are given the results obtained by the official method and the method here described, together with the percentage of nitrogen in nitrates as determined by the Schulze-Tiemann method.

The average of the twenty-five determinations by the Scovell-Jodlbauer method is 4.64 per cent, by the proposed method 4.65. The greatest discrepancy in any instance

* Contains 1.89 per cent nitrogen in ammonia salts.

† Contains 1.70 per cent nitrogen in ammonia salts.

‡ Contains 1.77 per cent nitrogen in ammonia salts.

is one-tenth per cent. In ten cases the proposed method gave the lower result, in thirteen cases the higher result.

	Nitrogen in nitrates by Schulze-Tie- mann.	Total nitrogen by Scovell-Jodbauer.	Total nitrogen by proposed method.
Pure potassium nitrate	—	13.73	13.71
Commercial nitrate of soda	—	15.86	15.90
Tobacco dust	—	1.76	1.71
Mixture of ground bone, muriate of potash, and nitrate of soda	3.61	5.74	5.66
Mixture of bone, tankage, disc. bone- black, mur. potash, and nitrate of soda	1.46	3.81	3.85
Mixture of bone, tankage, dis. bone- black, sulph. and mur. potash, sulph. am., and nitrate soda	0.63	4.15	4.07
Mixture of bone, tankage, dis. bone- black, sulph. and mur. potash, and nitrate of soda	0.43	4.03	4.10
Mixture of tankage, dis. bone-black, mur. potash, and nitrate of soda ..	2.23	4.41	4.51
Mixture of tankage, dis. bone-black, wood ashes, and nitrate of soda ..	1.63	3.85	3.85
Mixed fertiliser	0.56	3.82	3.86
"	2.39	6.89	6.99
"	0.69	4.84	4.89
"	1.55	3.45	3.47
"	0.36	3.05	3.10
"	0.86	2.70	2.65
"	1.54	3.56	3.63
"	0.21	2.84	2.79
"	0.83	3.69	3.76
"	0.12	2.83	2.77
"	0.95	4.84	4.91
"	0.70	2.48	2.44
"	0.68	2.56	2.56
"	0.38	3.56	3.55
"	0.91	2.54	2.58
"	2.91	5.02	4.96

THE ANALYSIS OF IRON AND STEEL.*

By JOHN PARRY, F.C.S., and J. JAS. MORGAN, F.C.S.

I.—INTRODUCTORY.

It requires only a moderate knowledge of chemical science to render one competent to carry out the general routine work of an iron and steel works laboratory. But it is of very great importance that the beginner should aim at becoming an expert and clean manipulator. Most of the methods of procedure hereafter described are very simple; yet the tyro will find that even the ordinary determination of carbon by the colour test cannot be done with anything like accuracy without considerable practice. And the same applies to the determination of the other elements—more especially phosphorus. All complicated and fragile apparatus are out of place, and fail to meet the needs of the iron and steel manufacturer, who requires tolerably accurate results, together with promptitude. The time consumed, together with the difficulty of keeping and maintaining delicate or elaborate instruments in perfect working order, and also the proportionately difficult manipulation, altogether forbid their use. The same may be said of the elaborate instructions given in an ordinary text-book on chemical analysis for weighing, drying, and transferring precipitates in their

entirety; they are useless in a practical iron works laboratory. In lieu of these operations, the steel works chemist simply folds up the wet filter paper containing the precipitate in the shape of a cone, and by gently blowing removes it from the funnel to the crucible, so that the base rests on the bottom, while the point is uppermost. He then places the crucible in the front part of the muffle until the combustion of the paper is complete, ignites immediately, withdraws, and cools quickly, generally by placing it on a thick iron plate, and covering with a glass shade. In nearly all steel works laboratories, directly ignition is complete, and the precipitate is sufficiently cool, it is thrown upon the pan. The counterpoising of crucibles is not practised, such operations being inadmissible through the time at his disposal being altogether inadequate. Were he to follow the routine generally described in text-books as regards the drying and burning of the filter paper and contents, the risk of error in his results would be considerably greater. As regards the employment of gas in the laboratory for igniting purposes, it certainly has many advantages, amongst them being that no risk from dust results from the use of the same as with a coke-fired muffle, a very great and important feature; while, again, its use may result in considerable economy. In a steel works laboratory, however, Bunsen burners for ignitions are too slow and altogether inadequate. A large muffle, heated by a coal fire, and through which a free draught of air circulates, should be employed. As regards weighing, most young chemists needlessly waste considerable time in this operation, forgetting that the results so obtained are covered by the experimental errors, which must occur in the course of chemical manipulation as practised under ordinary conditions. For practical purposes, it is useless to weigh nearer than one-half a milligram; while, in weighing large quantities, a limit of even a milligram may be allowed. It is of far more importance to become a clean and expert manipulator, to be able to pour out solutions to the last drop, as also to acquire the knack of transferring precipitates from one receptacle to another quickly and without loss, and to avoid the errors entailed by dirty apparatus. We have known instances in which these obvious sources of error have been quite ignored, the chemist consoling himself, when confronted with the discordant results so obtained, that these could not possibly be due to any fault of his, because he had always weighed the various portions of the sample taken for analysis, as also the resulting precipitates, with the greatest care, never allowing an error of one-hundredth of a milligram.

We have already stated that all complicated apparatus is altogether out of place in a steel works laboratory, which should be fitted up as simply as possible. The chief aim of the present day, however, seems to be to possess a laboratory which from an architectural point of view, leaves nothing to be desired either as regards design or fittings, but as far as the comforts of those who have to work in the same, or of its suitability as regards size and arrangement, is far from being perfect. In building a laboratory, the main object should be to obtain a large, well-ventilated and lighted room to serve as a general work room, with at least one good room fitted up for the reception of the balance, and also to serve as the library. This room should be made as dust-proof as possible, and in close proximity to the general work room or laboratory proper. The stove for heating the muffle should be so arranged that the firing is done in a room which would also serve as the store-room, while the muffle is in the balance room, and the top of the stove in the general room. The top of the stove should be formed with a hood and glass door to be used as a stench cupboard. In addition, the usual arrangements for gas burners should be fitted up in the laboratory at the convenience of the operator.

The methods, with the precautions to be observed, and given hereafter, are only applicable to the practical

* From *Industries*, August 30, 1889.

analysis of iron and steel, and as a rule only results of moderate accuracy are obtained. An exact scientific analysis either of iron or steel is altogether beyond the province of a practical steel worker; and for its successful application requires special scientific training to be obtained only in a laboratory devoted to physical and chemical research, under the tuition of a trained scientist. The main object of a works analysis is, as a rule, to keep the average chemical composition of the metal within certain known limits, so as to insure the production of a material, such as steel or iron, of average good quality, and free from any excess of injurious impurities; for it is quite impossible to always produce either pig iron or steel of exactly the same chemical composition. Unless, however systematic daily analyses are made, there can be no check on the manufacture, and in our experience the neglect of such analyses has always resulted in failure, attended with a serious pecuniary loss. We may remark also that the ordinary analyses of iron and steel, in which the silicon, carbon, sulphur, phosphorus, manganese, and sometimes copper and chromium, are determined, often fail to afford any explanation of the abnormal behaviour of certain samples when subjected to ordinary tests. So much is this the case, that many engineers and manufacturers are inclined to altogether ignore chemical analysis, and prefer relying solely on physical tests. While, on the other hand, others of equal repute advocate an extension, asserting that our ordinary analyses must be incomplete, and urging the chemist to search for some as yet unknown impurities, other than silicon, carbon, and sulphur, which may be present. A great deal of time and trouble has been expended on research of this class; but, on the whole, it may be said that the results so obtained have added very little to our present knowledge. It has been ascertained that both iron and steel always contain a notable proportion (by volume) of hydrogen and carbonic oxide gases, with smaller quantities of carbonic acid and nitrogen. It has not, however, been demonstrated that these gases affect the quality of the metal as such, or indeed whether they exist in combination with iron at all. They appear to only mechanically weaken iron, or more especially steel castings, by rendering them porous, the gases collecting in bubbles in the interior (causing what are technically termed "blow holes"), which consequently reduce the strength of the castings. Some chemists, however, assert that steel containing hydrogen is brittle; while others, on the contrary, hold that no difference can be traced between it and steel containing none. The same applies to nitrogen and carbonic oxide.

It has been shown that iron may contain, and indeed often does contain, other elements than those given in the ordinary analysis; but the enormous difficulty of absolutely quantitatively determining their presence, and freeing them from the great preponderating bulk of iron through which they are diffused, causes some to be sceptical as to the results given, to say nothing of the extreme care required to insure the complete isolation of the material undergoing analysis from external contamination, such as would accrue from the employment of impure chemicals, the doubt as to the absolute cleanliness of the apparatus, and last, but not least, the danger of contamination arising from the fact that the glass and porcelain vessels cannot be said to be absolutely insoluble in the strong acids and reagents used. Indeed, some of our best and most reliable chemists assert that it is impossible to avoid error from this latter cause, and that therefore all analysis should be performed in platinum vessels, and glass and porcelain be altogether discarded.

To avoid the manipulative difficulty of dealing with the immense masses of iron, as compared with the minute quantities of foreign ingredients presumably present, and the uncertainty of the complete separation of these by precipitation in the presence of an excess of metal, it has been proposed to reverse the usual process of endeavouring by precipitation to separate the impurities

from the iron, viz., to extract the foreign matter by digesting the mixed impure mass in suitable solvents. By this method copper, nickel, cobalt, magnesium, chromium, aluminium, calcium, and lead have been detected in steel by simply heating 10 ozs. of the metal with nitro-hydrochloric acid, evaporating nearly to dryness, digesting the pulpy mass with (1) water, (2) ammonia, (3) acetic acid, (4) sulphide of ammonium. The solutions are mixed together, evaporated to dryness with a small quantity of hydrochloric acid, re-dissolved, and upon subsequent examination are found to contain the above named elements, together with a small quantity of iron, which consequently renders analysis by the ordinary precipitation methods easy. This method has the further advantage that a quantity, utterly unmanageable when treated by the ordinary methods, may be taken for analysis; and further, that sensible quantities of the various impurities are obtained for weighing and examination. This work, however, up to the present has given little as regards results, and the quantities thus determined have, with a few exceptions, been found so minute as to lead many to doubt their efficacy either for good or evil.

It is probable that we have much to learn, and if we are satisfied that these bodies are contained in iron, it may, on the whole, be best to await further investigations. If, however, we admit that both iron and steel may contain minute proportions of these elements, it cannot be said that in the face of the fact—viz., that, as regards other metals, the introduction of a very minute proportion of some foreign ingredients is sometimes deleterious—these minute quantities can have no effect on iron and steel—we simply do not know. A well-known metallurgist has stated that the research for and determination of substances technically termed impurities of iron is nearly over, and that we have little left for research, except the so-called pure iron itself, which, after all, may be a compound body. Others assert that iron, in the form of an alloy, or in combination, is a very different material from iron as such. The study of the higher chemistry shows that it is probable that so-called "elements" are derived from one primary body; elements may be neither more nor less than equivalent quantities of this primary body. Crookes states that the rare earths such as didymium and yttrium, show a close mutual similarity in members of the same group; and yet, by his method of analysis, distinct differences have been tabulated, which the ordinary analytical methods failed to indicate. Should this be the case as regards so-called pure iron, it is evident that a wide field for further investigation is before us; and the fact that those who have made the study of iron their speciality are almost unanimously agreed that they have not seen, and have failed to manufacture, absolutely pure iron, renders it probable that it is so. Possibly, work done in this direction may afford a reasonable explanation of the fact which cannot now be longer ignored, viz., that physical tests often give results not at all corresponding to those inferred from the ordinary chemical analysis, and, indeed, these discrepancies have become so marked that it has been suggested that iron is possessed of some unknown property beyond the scope of analysis. This seems, in our opinion, a step in a backward direction, which, even with our present confessedly imperfect knowledge, cannot for a moment be allowed. We may be excused for saying that all this may have little or nothing to do with the metallurgical chemist of the future. It seems that the task before him is: (1) If iron be a compound body, to isolate and give the proportionate quantities of this problematic compound; (2) if iron undergoes, or partly undergoes, a molecular change, such as is well known to occur with other bodies, to isolate, as has been done with other substances, the iron molecularly changed, and of more importance still, to tell us whether iron is a body partly composed of iron as such, combined or intimately mixed with molecularly changed iron. It follows that for all practical purposes

it comes to the same thing to say that iron is a compound body, or that it has undergone a partial molecular change. The relative proportions of each must be isolated and weighed in the balance.

We know that in the case of metallic oxides, also of some of the metals and metalloids, under certain conditions they undergo allotropic change. In some instances a simple elevation of temperature suffices, and in the case of alloys Professor Roberts-Austen shows that modifications may be induced, rendering one portion of the alloy less soluble in acids than the other. (We would add here that the Cantor Lectures on Alloys, by Professor Roberts-Austen, are well worth reading, and convey a mass of information which should be studied by the practical metallurgist.) We may say that tin is capable of undergoing such an allotropic change: (1) a state in which it is hard and brittle, sp. gr. 6; (2) one which is malleable, sp. gr. 7.16; and many other instances might be quoted, and all quite familiar to the ordinary student. We repeat, that the analytical chemist must not, however, be content with mere words or formulæ when, say, a metal such as steel takes the form of, in one instance, a hard brittle substance, and in the other remains soft and malleable. It rests with him to determine by the balance whether these contrary effects are due to the introduction of foreign elements or, as before said, to molecular changes. In urging the chemist to investigate it must not be inferred that we indorse all that has been quoted on molecular change or difference; we can only say that such changes may occur, that further investigation is needed, and that a promising research is before him. Iron may exist in a more or less condensed state; in other words, its atomic weight may vary within certain narrow limits. Indeed, Crookes states that this is probable in the case of some of the elements. Another field for investigation, which may be termed practically feasible, arises from the results of a series of laborious microscopical studies of the fracture of various qualities of iron and steel, formulated by Dr. Sorby. (For the complete article on "Microscopical Structure of Iron and Steel," see *Journal of Iron and Steel Institute*, Part I., 1887.) Briefly, this operator has shown that iron and steel are not, as usually assumed, homogeneous, but rather heterogeneous bodies, which he classifies as follows:—(1) Free iron; (2) iron combined with carbon, an intensely hard compound; (3) pearly constituent compound of Nos. 1 and 2; (4) the pearly constituents, re-crystallised; (5) ruby-coloured crystals; (6) graphite; (7) slag; (8) slag and undetermined residue; (9) soluble metallic substances; (10) metallic substances less soluble; (11) schreibersite. It follows, therefore, if we accept Dr. Sorby's results in their entirety, that the elementary analysis of the metal, giving only graphite, combined carbon, sulphur, phosphorus, &c., can only furnish limited information, and should be supplemented, or even replaced by proximate analysis. The task before the chemist is to isolate these various compounds, and gravimetrically determine the percentage of each. It is now considered all but certain that neither iron nor steel is perfectly homogeneous; consequently many chemists have devised sundry methods for the separation of their constituents. Much, however, remains to be done, as a good all round method of proximate analysis has still to be devised.

(To be continued).

Nerve Tissues of Certain Invertebrate Animals.—Dr. A. B. Griffiths.—In the nervous tissues of insects and crustaceans, neurokeratine is replaced by neurochitine. The matter of the nerves of the lower animals is very unstable. When fresh it is slightly alkaline, but becomes acid shortly after death.—*Comptes Rendus*, cxv., No. 16.

ON IRON RUST POSSESSING MAGNETIC PROPERTIES.*

By A. LIVERSIDGE, M.A., F.R.S.,

Professor of Chemistry in the University of Sydney.

My attention was first drawn to this matter in January, 1889, when walking along the pier at Clifton Springs, Port Arlington, Victoria, by noticing the large scales of rust attached to the old tram rails, which had not been in use for some years. On breaking off fragments I was much struck by their resemblance to the crust seen on many metallic meteorites. Some of the pieces were from a quarter to one-third of an inch through, one to two inches wide, and three to four inches long. Although retaining somewhat the form of the original iron they were very brittle, and, on breaking them across, the fracture had a slight resemblance to that seen in some non-crystalline magnetites. Further, on scraping the rust and breaking pieces off with a pocket-knife, the dust and fragments were strongly attracted to the blade which had been magnetised. I could see no traces of metallic iron, and felt sure that practically there were no particles of the metal in the rust. I could not, of course, make quite certain without other appliances, so on my return to Sydney I examined the rust carefully for metallic iron by grinding it in an agate mortar, but could not find the smallest speck of metal; the material ground readily to the last portion and yielded a dark brown coloured powder, and, to my surprise, I found the powder to be *wholly* attracted by the magnet, and not merely in part as I expected. I did not care to publish the above as it rested upon observations made upon a single specimen, and was directly opposed to the usual statements in text-books and works of reference on chemistry, that rust is a non-magnetic hydrated sesquioxide of iron, and an opportunity to proceed with the matter did not occur until September last.

It may be thought that more has been made of the matter than its comparative unimportance warrants, but as my results are at variance with the general statements placed before students and others (statements which are of many years' standing), it is perhaps not unjustifiable to place sufficient evidence on record to establish the facts and place them on a firm footing. Fortunately the statements can be verified by anyone possessing a magnet, no matter how poor a one it may be, inasmuch as material can be obtained from any old piece of rusty iron.

Since then I have been able to examine other specimens of rust and to make a few experiments upon the matter, all of which bear out the original observation and show that ordinary iron rust is usually attracted by the magnet.

By magnetic rust or oxide in this paper is meant iron oxides, which are attracted and lifted by a small bar magnet of one-eighth of an inch in diameter, or by an ordinary penknife blade which had been magnetised; but when seeking to separate large quantities, a bar magnet which would lift four ounces of iron or an electro-magnet lifting eighteen ounces was employed. As mentioned in a preceding paper, a powerful electro-magnet was considered inadmissible.

In spite of all the care exercised in grinding and using the magnet under water, there may still be some non-magnetic oxide mechanically enclosed and carried over by the magnetic particles, as is seen when it is attempted to separate sulphur and iron filings by a magnet; but from the number of times that the same powder can be lifted without leaving anything behind I think it cannot amount to much, and may be neglected as unimportant.

The source of the iron rust and the conditions under which it had been found are given in what might appear

* From the *Transactions of the Australasian Association for the Advancement of Science*, Hobart Meeting, 1892.

as unnecessary detail, but full particulars are furnished so that it may be seen that iron of various qualities, *e.g.*, common, cast, inferior, and the best malleable iron and steel all furnish rust containing magnetic oxide in the early stages of the rusting, and that under certain circumstances the final products—the sesquioxide and hydrated sesquioxide of iron—may also be magnetic.

Metallic iron was found in every case by careful examination for specks of metal when grinding in the agate mortar, and also by digesting the powder in a solution of iodine in potassium iodide for some hours, but proved to be absent except in one or two cases, which are mentioned further on.

No. 1.—*Rust from Iron Rails: Clifton Springs, Port Arlington, Victoria.*

This specimen was collected, as stated above, in January, 1889, from the old tramway on the pier at Clifton Springs, Port Arlington, Victoria.

9.1 grms. were crushed and sent through a No. 60 sieve. The dark brown powder was wholly attracted by the magnet, the amount of non-magnetic powder left after repeated applications of the magnet being almost invisible. The attempted separation of any non-magnetic matter was repeated time after time, so as to get rid of any entangled non-magnetic dust, but always with the same result.

The rust was also acted upon by the magnet under water, after re-crushing to an impalpable powder in an agate mortar. This was done to avoid as far as possible non-magnetic oxide being lifted mechanically between or by attached particles of magnetic oxide; but after many repeated attempts to obtain non-magnetic rust from it, I had to come to the conclusion that it was all attracted by the magnet.

Another attempted separation was made on 5.640 grms. powdered in an agate mortar, but with a like result, *i.e.*, the whole was attracted.

These scales of rust were found to be not only magnetic, but some were also polar, *i.e.*, they not only attracted one end of the magnetic needle but also repelled the other, and the opposite edges of the fragments possessed opposite polarities; moreover, when suspended in a stirrup by unspun silk some specimens set themselves in the magnetic meridian, a further proof of their being magnetic and not merely lumps of ordinary rust containing particles of metallic iron.

The specific gravity was found, by Joly's apparatus, to be 4.07 at 18°, native magnetite being 4.9 to 5.2.

A portion of this rust yielded 70.11 per cent metallic iron (by the bichromate volumetric process), the theoretical amount in magnetic oxide, Fe_3O_4 , being 72.41 per cent.

To confirm, or otherwise, the results obtained from the old rail, rust specimens were collected from various sources, and these on examination verified the previous observations in almost every particular.

The rust in each case was scraped off with a horn spatula and crushed in a porcelain mortar, and the precautions taken were such as to prevent any metallic iron finding its way in; further, the magnetic powder was in every instance proved to be free from any particles of iron.

No. 2.—*Rust from an Old Iron Waggon lying on Lady Robinson's Beach, near Sydney.*

The scales are about one-eighth of an inch thick, and come off in large flakes five or six inches across. On the outside, as well as the inside (*i.e.*, next to the still unoxidised iron of the waggon), they present the usual appearance of rust, being scaly, and of a dark brown colour with light ochrey patches, with here and there a small cone-like excrescence. Specific gravity at 16° C. = 3.76.

On breaking the scales across they present a dark—

almost black—coloured interior with a well marked fibrous crystalline structure, such as is seen in many Goethites. This internal part gives a dark brown streak or powder, the outer film gives a pale ochre-coloured powder. The rust is picked up bodily by a magnet—whether a magnetised knife-blade, a horse-shoe, or electro-magnet is used—and some of the scales show well-marked north and south poles. On being crushed it yielded a dark brown powder, which was found to be wholly lifted or attracted by a magnet, *i.e.*, no non-magnetic portion could be obtained from it.

In one case 409 grms. were crushed and sent through a No. 30 sieve; only one grm. was left by the magnet, and this was seen to consist of rounded grains of sand from the beach.

Another portion was crushed and sent through a No. 60 sieve; this likewise was wholly attracted by the magnet.

A third portion was scraped on both surfaces before crushing. The outer crust or scrapings—5.25 grms.—gave a yellowish brown-coloured powder, which was wholly lifted by the magnet; the inner dark and crystalline part, weighing 432 grms., gave a brown powder, and was also entirely magnetic.

Cakes of this and other rusts, 1th to $\frac{3}{16}$ ths of an inch, and of three or four inches superficial area, are drawn to a horse-shoe magnet capable of sustaining a pound weight of iron, with a slight jump like pieces of thin sheet-iron, but with, as might be expected, very much less readiness.

No. 3.—*Rust from an Old Wrought-Iron 400-gallon Water-Tank, made of thin "boiler" plate, and used for shipping malt to Sydney.*

Specific gravity = 3.90 at 18° C. This had the usual appearance of rust scales, but was strongly magnetic. Distinct north and south poles were shown by some of the large pieces; 13.3 grms. were crushed and sent through a No. 60 sieve; the brown powder was wholly lifted by the magnet. A second sample, weighing 10.545 grms., was also found to be wholly magnetic.

Another fragment or scale was crushed in an agate mortar, and 10.205 grms. of an impalpable brown powder obtained. This was placed in a glass spitz-kasten (or Knop's soil-washing apparatus), and separated into three portions of different specific gravities, but all were found to be attracted by the magnet.

The yellow ochre-like superficial rust from some of these scales, 8.096 grms. in weight, was ground to an impalpable powder and dried in a water-oven; and even this was wholly attracted by the magnet, although feebly.

No. 4.—*Rust from an Old Flue Pipe, but which had never been used.*

Some of this was powdered and sent through a No. 60 sieve; the light brown coloured powder yielded 2.25 of strongly magnetic and 2.3 grms. of feebly magnetic powder.

No. 5.—*Rusts from Old Bolts, Bars, &c., which had been lying exposed to the weather in a wooden box.*

Of the usual "rust colour" and appearance. The powder yielded—Magnetic particles, 7.71 grms.; non-magnetic particles, 0.205 grm.

No. 6.—*Rust from Old Wrought-Iron Tyre.*

Weight of powder = 4.691 grms. In separating this under water a certain amount of fine powder was obtained in suspension, and this apparently was not attracted; at any rate it could not readily be removed from the water by the magnet, but on evaporating it down on a sand bath it was found to be wholly lifted by the magnet.

Another specimen of the same, weighing 9.856 grms., was crushed in an agate mortar, dried in water-oven, and also found to be wholly lifted by the magnet.

No. 7.—*Rust from Old Sheet-Iron Barrow*, probably formerly galvanised.

The scales showed well-defined north and south poles. 146 grms. were crushed and passed through a No. 30 sieve. The whole of the dark brown powder was found to be attracted by the magnet.

No. 8.—*Rust from Old Disused Boiler-Plate Chimney*.

60 grms. were crushed and passed through a No. 30 sieve and yielded a dark brown powder, the whole of which was magnetic. The scales were also polar.

This example is not of so much value as the others, because it might be thought that the scale consisted of or contained magnetic oxide (Fe_3O_4), which had been formed at a high temperature, although personally I am satisfied that it was formed by the ordinary process of atmospheric rusting.

No. 9.—*Rust from Old Tinned-Iron Can*.

All traces of metallic tin had disappeared. 16 grms. were crushed and passed through a No. 60 sieve; the light brown powder was wholly lifted by the magnet.

No. 10.—*Rust from Scrap Heap*.

In the form of cakes, from $\frac{1}{16}$ th to $\frac{1}{8}$ th of an inch in thickness, and of several inches superficial area. The cakes were of the usual dark brown colour, but with soft powdery yellow-ochre patches and cones or excrescences. These were detached and ground separately in an agate mortar, and found to be nearly free from magnetic particles, but the soft black powder found under the excrescences or pimples was highly magnetic.

No. 11.—*Rust from Flat Iron Bars*.

These had been left lying on the ground exposed to the weather; the whole of the rust was highly magnetic.

(To be continued.)

NOTICES OF BOOKS.

Chemical Lecture Experiments. Non-Metallic Elements.

By G. S. NEWTH, F.I.C., Chemical Lecture Demonstrator in the Royal College of Science, South Kensington. London and New York: Longmans, Green, and Co. 1892. 8vo., pp. 324.

THE aim of this work, as we are told in the preface, is twofold. It is to supply chemical lecturers and teachers with a selection of experiments suitable for illustrating the preparation and the properties of the non-metallic substances. Secondly, it is to serve the student as a companion to the lecture-room, giving the details of the experiments which he is likely to see performed, and saving him the trouble of taking notes and of sketching apparatus. It will be at once evident that the experiments are well selected and fully and clearly described. The illustrations scarcely leave anything to be desired.

Critical and dangerous experiments have been intentionally omitted. Like those which show the action of substances upon animal life, they are best committed not to the student but to the "researcher,"—if so questionable a word may be used.

Mr. Newth tells us that whilst adopting the metrical system, he has added the English equivalents of the French measures of length. The sole reason why the metric system of weights and measures has not long before this become dominant in England is its nomenclature, utterly repugnant to the genius of our language.

An interesting experiment has been devised to show the part played by suspended matter in that unhappy task the formation of fog. Mr. Newth's work is admirably adapted for students attending courses of lectures on inorganic chemistry.

A Short Manual of Analytical Chemistry, Qualitative and Quantitative, Inorganic and Organic. Arranged on the principle of the Course of Instruction given at the South London School of Pharmacy. By JOHN MUTER, M.A., Ph.D., F.R.S.E., F.I.C., F.C.S., &c. Fifth Edition, Illustrated. London: Messrs. Simpkin, Marshall, and Co., Ltd., and Messrs. Baillière, Tindall, and Cox. 8vo., pp. 212.

THIS manual, which may boast of having now reached its fifth edition, is fully worthy of the reputation which it has earned. Dr. Muter, much to his credit, tells us that his treatise is not intended to be a mere "examination book." It differs from the general run of the ordinary analytical manuals in including a number of the most important organic substances, instructions for the analysis of water, foods, and drugs, for colorimetry, and for the application of the polariscope and the spectro-scope. On the other hand, we must admit that some of the elements—those chiefly of little interest in pharmacy—have been excluded.

The chapter on the detection of alkaloids and on toxicological procedures is very ably written. Its chief defect is the omission of two very formidable poisons, aconitine and atropine. For this defect, however, Dr. Muter is not to blame. These substances, as he reminds the reader, can only be certainly detected by experiments on animals,—a method which is not only "a grievous sin," but illegal, save under a special licence not always to be obtained. In fact, to many toxicologists it would be easier to run over to Calais and to perform the experiments there.

Gas-analysis is here rather briefly noticed, but the student is referred for all necessary details to Sutton's well-known "Volumetric Analysis." We have no doubt that the present edition of Dr. Muter's work will still enjoy the favour which competent authorities have awarded to its predecessors.

Everybody's Writing-Desk Book. By CHARLES NISBET and DON LEMON. London: Saxon and Co.

WE have here a very curious, but we must at once admit, an exceedingly useful book. The introduction contains a most valuable suggestion:—"It is a good rule, so far as practicable, to watch the times and the seasons, and take pen in hand only when the subject is in the ascendant." But the man of Science generally labours under the disadvantage that none of his subjects is in the ascendant.

Contrasting work which is slowly and patiently elaborated with that which is a spontaneous outburst, the authors evidently seem to award the palm to the latter; but in some subjects such rapid utterances are out of the question. A writer like Darwin, busy up to the last moment in weighing the results of new experiments, new observations, and new criticisms, cannot dash off his theories as the poet, the divine, or the novelist may pour forth his master-pieces.

The authors call attention to the following points as to be observed in writing: (1) arrangement; (2) compass; (3) words and their mutual congruity. Few, we fear, after seeing how these points are here worked out will fail to see that they have been not un-frequent transgressors in these important respects. But there is one class of defects in modern writings which Messrs. Nisbet and Lemon seem to have overlooked. We find no protest against the use of words taken in an illegitimate meaning, vulgarisms, slang expressions, and Americanisms. It is distressing to find "phenomenon" used to signify something unheard of; yet this error, originally confined to the advertisements of strolling actors, has become epidemic and has even attacked the medical papers. Among Americanisms the authors would have done well to denounce the verbs "to donate" and "to loan"—expressions as needless as inelegant, yet unfortunately "going the round of the papers."

The section on "synonyms and antonyms" will prove exceedingly useful. A writer, whilst possessing perfectly clear ideas, may often have to pause for the most suitable manner of expression. Here the "Writing-Desk Book" will often come to his aid. We must, however, beg to protest against "fragile" and "weak" being accepted as synonyms for delicate. If a person in bad health is spoken of as "delicate," one who is perfectly sound may be pronounced "indelicate." Of this a remarkable case is on record. A lady, speaking of her nephew, said "when he was little we all feared he would be very delicate, but now he has got into his teens he is as indelicate a boy as you could find in a day's journey."

A few vulgarisms have found their way among the synonyms. "Gabby" is surely not to be recommended as a synonym for talkative.

Science Instruments. Catalogue of Scientific Apparatus and Reagents. Manufactured and Sold by Brady and Martin, Northumberland Road, Newcastle-upon-Tyne, and at 29, Mosley Street. 1892.

WE are sometimes told that our predecessors, Scheele, Davy, Wollaston, and others, obtained admirable results without that plethora of appliances which figure in modern catalogues. With gallipots and saucers, crucibles and tobacco-pipes, they made capital discoveries. Hence it is asked why cannot we do the same? In reply to this insinuation we remind the objectors that it was just the same with gold-digging in the early days of Australia and California. With a spade and a pickaxe, a dish and a bucket, the digger brought to light grains and nuggets in abundance. But this state of things has come to an end. The alluvial deposits are exhausted, and they who would now obtain gold must be prepared to grapple with quartz-reef, and bring to bear chemical and mechanical skill backed up with no inconsiderable capital before they can secure the precious metal.

In chemical research the case is precisely the same. The facts and the conclusions which lay near the surface have already been made known, and to effect any advance in Science we must have at command instruments of precision such as we find figured and described in the excellent catalogue before us. Here we see a full and judicious assortment of apparatus to meet the requirements of the student, the analyst, and the man engaged in original research. Whether as a nation we are really advancing in experimental Science is, perhaps, not absolutely certain, but the demand for apparatus, chemical and physical, is largely on the increase. It is also plain that the instruments offered are improving in quality.

Apparatus for gas-analysis figures more and more largely in the catalogue of dealers, as it is well shown in the list before us. Filter-pumps also are becoming more and more appreciated. Bacteriological apparatus, so imperatively needed in sanitary analysis, figures here largely and includes the most improved instruments.

In the list of microscopes we notice what is apparently a curious typographical error. Under Beck's laboratory microscope (No. 754) we notice that it is fitted with an "Irish diaphragm." This, we presume, should have been "Iris diaphragm."

Physical and meteorological appliances are also not omitted. Three different spectroscopes are figured. Even anthropometric apparatus is here given, the writers pointing out the grave importance of such measurements and registrations.

The catalogue of reagents and chemicals presents a novelty which seems to us very useful. Many of the rarer chemicals are not quoted, but we are informed in a note that they can be supplied on application. This catalogue will be found very useful to the chemist and the student by aiding them in the selection of apparatus which they may require for any purpose. The prices quoted are decidedly reasonable for accurate, trustworthy instruments, and for pure reagents.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 16, October 17, 1892.

Reaction alleged as Peculiar to Spermine.—M. Duclaux.—If spermine possesses energetic curative properties, the properties are absolutely independent of its action upon magnesium in presence of platinum or copper chlorides.

Novel Preparation of Acetylene.—L. Maquenne.—The author decomposes crude barium carbide by cold water, which is added drop by drop so as to avoid a too sudden heating of the mass. The acetylene is given off regularly at a speed proportional to that of the afflux of the water, and it may be at once passed into the apparatus in which it is to be used. One hundred grms. of the barium carbide give from 5200 to 5400 c.c. of gas containing from 97 to 98 per cent of acetylene, and 2 to 3 per cent of hydrogen, with an appreciable admixture of any other hydrocarbon. If this gas is slowly passed through a long glass tube at a dull red heat it yields in the course of a day several grms. of synthetic benzene.

Analysis of Mixtures of Ammonia and of Methylamines.—H. Quantin.—This paper will be inserted in full.

MISCELLANEOUS.

Sewage Pollution.—The town of Bury (Lancashire) has been fined £20 for polluting the river Irwell. The daily output of sewage at Bury has amounted to one million gallons. Further offences will be more strictly dealt with.

Index to the Literature of Explosives.—The manuscript of Part II. of the "Index to the Literature of Explosives," by Charles E. Munroe, Torpedo Station, Newport, Rhode Island, U.S.A., is now ready for printing, and, provided a sufficient number of subscriptions are obtained in advance to warrant doing so, it will be issued in pamphlet form, of approximately 150 octavo pages, at 1.00 dollar per copy. Part I., issued in 1886, contains the titles of all articles relating in any way to explosives that appear in—

American Journal of Arts and Science ..	1819—1886.
Philosophical Transactions of Royal Society ..	1665—1882.
Journal of Royal United Service Institution ..	1857—1885.
Proceedings U.S. Naval Institute	1874—1885.
Revue D'Artillerie	1871—1884.
H.M. Inspectors of Explosives Reports ..	1873—1885.

Part II. continues the index for the above periodicals up to 1891, and contains the following in addition:—

Dingler's Polytechnisches Journal	1820—1890.
Proceedings American Chemical Society ..	1879—1890.
Nicholson's Journal	1797—1813.
Popular Science Monthly	1872—1890.
Edinburgh Journal of Science	1824—1832.
Brande's Journal of Science	1816—1830.

This index has been made by a careful search of each page of each of the 984 volumes included in it, and is believed to be complete from the date of first issue of each of the periodicals named.

New Process of Producing Caustic Soda, &c., from Brine by Electricity.—The *North-Eastern Daily Gazette* (Middlesbrough) announces a new discovery which it regards as potentially "second only in importance to

the North of England to John Vaughan's famous opening up of the Cleveland ironstone." It is the discovery of a new and simple process of producing caustic soda, chlorine, and other chemical products direct from the brine by electricity. The most careful tests applied up to the present time show, says the *Gazette*, an economy of over 50 per cent as compared with present methods. It is described as the simplest of all the known processes of soda making, the caustic soda being produced direct from the brine in one operation instead of two. At present carbonate of soda is first produced, and from that the caustic soda is made. "The valuable chlorine is also saved and utilised for the production of bleaching-powder and other by-products." Eminent chemists and electricians have already pronounced the new method a complete success from a chemical point of view, and it is said that there is every prospect of its being worked as a commercial success. Our contemporary regards it as of the greatest promise for the future of the North of England, which is at present too much dependent on the iron trade alone.

MEETINGS FOR THE WEEK.

MONDAY, NOV. 7.—Royal Institution, 5. General Monthly Meeting.

FRIDAY, NOV. 11.—Physical Society, 8. Continued discussion of the papers by Mr. Williams and Mr. Sutherland, "Dimensions of Physical Quantities" and "Molecular Forces."

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1720.

VOLATILE FATTY ACIDS OF BUTTER.

NOTE ON A RECENT PAPER BY WILLIAM JOHNSTONE.

By H. DROOP RICHMOND.

IN the CHEMICAL NEWS, vol. lxvi., p. 188, appears a paper entitled "Volatile Fatty Acids of Butter," in which the author draws the conclusion that "the solid fatty acids which collect in the condenser (during a Reichert-Wollny distillation) consists (*sic*) of—

18.6 per cent of pseudo-oleic acid,
81.4 " " myristic acid."

In a previous paper (*Analyst*, xvi., 26) he had shown that they were mainly capric acid, a conclusion which he has to all appearances abandoned.

There is in the paper strong internal evidence that his conclusion is unwarranted. After following the method I have previously found necessary with papers by this author, and correcting the mistakes in simple arithmetic, and translating his language into readable English, I find his procedure to have been as follows:—

He distilled the solution obtained by treating 5.433 grms. of butter-fat (probably not butter) according to Wollny's directions, and presumably collected 110 c.c. of distillate; at this stage he obtained 0.273 grm. of fatty acid by presumably washing out the condenser tube, and washing and drying the fatty acids therein. This quantity was used up for a determination of the iodine absorption, the figure found being 16.74 per cent iodine absorbed.

Water was then added and the distillation proceeded with until the flask (or retort) broke; the quantity of fatty acids obtained was 0.332 grm., and more would probably have passed over had not the accident occurred.

The total quantity collected was, then, $0.273 + 0.332 = 0.605$ grm., or 11.14 per cent (not 0.506 grm., or 9.31 per cent). The second fraction of 0.332 grm. was converted into a barium salt, of which 0.355 grm. (if the weight of the salt dried at 100° is assumed to represent the weight of the dry barium salt, or 0.354 if that dried at 130° is so taken) was taken and gave 0.136 grm. of barium sulphate by ignition with sulphuric acid; the barium salt is then equivalent to 0.276 (or 0.275) grm. of fatty acid; as the author evidently takes the weight of the salt dried at 100° to represent the weight of the dry salt, I follow him. Out of his total of 0.605 grm. of fatty acids collected, he has used 0.273 to determine the iodine absorption, and 0.276 to determine the barium in the barium salt; this leaves only 0.056 grm. for further examination, even if we admit that nothing was lost in the various operations.

He then took a further portion of his acid (of which only 0.056 grm. were available), converted it into a lead salt, washed it with alcohol, and thoroughly extracted with ether; he decomposed his lead salt, took the melting-point of the fatty acid thus obtained, dissolved it in alcohol, and converted it into an ammonium salt; from this he prepared a silver salt. Assuming that nothing was lost in manipulation and that only 20 per cent was soluble in ether (a low figure, seeing that the extraction was thorough), the total possible quantity left could not exceed 0.045. He, however, finds 0.456 grm. of silver salt, which contain 0.1465 grm. silver, and are therefore equivalent to 0.311 grm. of fatty acid; this fatty acid he shows to be myristic acid by a silver determination in the silver salt and the melting-point.

He has therefore succeeded in synthesising 0.266 grm. of myristic acid; there is strong evidence that it is syn-

thetic on account of the extreme purity of the acid, shown by the agreement of the melting-point found, 53.2° , with that given by Kraft, 53.8° , for the pure acid; had the acid been naturally existing and separated by the procedure he followed, it would not have been nearly as pure.

By means of a little juggling with figures and formulæ he is enabled to conclude from a determination of the iodine absorption on one fraction, and a determination of the properties of a substance evolved during the treatment of a second fraction, that the solid fatty acids collected consist of—

18.6 per cent of pseudo-oleic acid,
81.4 " " myristic acid.

He gives no clue as to how he identified "pseudo-oleic" acid, a substance whose properties are not yet generally known; he does not say whether it is the same compound previously described by him (*loc. cit.*) as "iso-oleic" acid. The publication of his researches on this compound will be interesting.

His conclusion must be considered as, to say the least, unwarranted by his experiments.

He presumably distilled further quantities of this butter-fat in the same manner, and examined the soluble volatile acid; he now finds notable quantities of acids of molecular weight higher than butyric acid in the distillate, while in the paper cited he found only butyric acid, and in a former paper (*Analyst*, xiv., 113) he mentioned propionic, acetic, and formic acids. There is hope, then, that in a few years he may find the same results as other observers.

50, Clanricarde Gardens, Bayswater, W.,
October 22, 1892.

ON THE LIQUEFACTION OF GASES BY ELECTRICITY.

By H. N. WARREN, Research Analyst.

THE usual method employed for rendering a gaseous body liquid, such, for instance, as chlorine, sulphur dioxide, &c., is as well known, prepared either by the action its own pressure exerts when evolved in a confined space, or by artificially lowering the temperature of the same, or thirdly, by a combination of both.

A brief description of the electrolytic method will, therefore, suffice to explain the strong analogy that exists with respect to both methods, save that at present the latter method is better adapted when a compound gas is desired, such, for instance, as HCl, &c. The apparatus employed consists solely of a stout glass combustion-tube, bent at right angles, and closed at either extremity, the longer limb containing two small platinum plates fused into the extremity of the tube, the bend of the tube containing a small plug of asbestos, soaked or saturated with strong H_2SO_4 for the purpose of retaining moisture. For the preparation of liquid HCl a sufficiency of a strong solution of HCl is introduced covering the platinum plates, and the asbestos plug inserted in the bend of the tube. The other extremity, being accurately sealed, is introduced into a freezing mixture of ice and salt.

To the outer extremity of the platinum plates, which should for convenience sake terminate in the form of wire, is connected a voltaic battery capable of quickly decomposing the acid. Large volumes of hydrogen gas, together with chlorine, are at once evolved, and becoming confined in the smaller end of the tube, aided by the low temperature produced by means of the freezing mixture, the gaseous HCl rapidly assumes the liquid form, the liquid thus produced being of a deep yellow colour, and often crystallises, due to the excess of chlorine present. If now the tube and its contents are withdrawn from the freezing mixture and the circuit discontinued,

the liquid gas is quickly reabsorbed by the water, forming a highly chlorinated solution, which experiment may be again performed as before; a number of other similar gases may be also thus liquefied.

An interesting reaction is also afforded when acidified water is substituted in place of the HCl solution, the condensing part of the apparatus being also provided with a very thin platinum plate, to the surface of which is attached some platinum black. On re-connection with the batteries, the usual decomposition of the water takes place, and the partially liberated gases, owing to the intense pressure they are exposed to, together with the surface action afforded by the presence of the finely-divided platinum, explode at intervals, each time generating small quantities of water, which was found on examination to contain large quantities of H_2O_2 , besides retaining most obstinately the powerful odour of ozone.

The above reaction may be made altogether more striking, and affords an excellent lecture experiment, by employing a small quantity of water containing a few drops of chromic acid, to which a sufficiency of ether has been introduced, and intended to form a layer upon the surface; the ether quickly assuming a deep blue colour, due to its absorption of the well-known blue oxide of chromium. By substitution of the acidified water, various other compounds, such, for instance, as acetylene, may be readily formed. For the liquefaction of oxygen and hydrogen gas, a modified condensing arrangement is being constructed, and the author hopes before long to be able to communicate to these pages explicit details concerning the same.

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NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.

(Continued from p. 225).

PFLÜGER, like Kjeldahl, calls attention to the fact that in very dilute solutions the free acid liberates an equivalent quantity of iodine with extreme slowness. The liquid mixed with solution of thiosulphate until the iodine colour disappears is coloured yellow again by the separation of iodine. The process lasts for many hours, and seems to come to no conclusion. Hereby larger quantities of iodine are liberated than that equivalent to the acid to be determined. Hence the supposition upon which the method is founded is inaccurate, as there is no certain indication when the action is completed, and the liberation of iodine is occasioned by other causes.

The experiments of Pflüger prove indeed that mixtures of potassium iodides and iodates permanently decompose each other by liberation of iodine, but this decomposition is so slight that for twenty-four hours it may be put = 0. Pflüger has removed the evil that the titration in very dilute solutions takes longer time by using a sufficient excess of iodide and iodate. If about 5 c.c. of sulphuric acid (1 c.c. = 0.001 grm. N) have to be determined in a dilution of about 500 c.c., the titration is completed in about a quarter of an hour, if the liquid to be titrated is mixed with 10 c.c. of a 20 per cent solution of potassium iodide and 13 c.c. of a 4 per cent solution of iodate. The quantity of solution of thiosulphate consumed in a quarter to half an hour indicates exactly the quantity of iodine equivalent to the free acid, so that even at an extraordinary dilution perfectly useful results may be obtained under the above-mentioned conditions. These directions, however, are valid only if ammonium salts are absent.

Continually occurring separation of iodine is consider-

ably increased in dilute solutions by the presence of ammonium salts, especially if iodine salts are present in larger quantities. The explanation of this circumstance must be sought in the fact that in presence of ammonium salts ammonium iodide and iodate are formed, and that in a solution of both these salts a continual separation of iodine occurs, which is especially energetic in concentrated solutions. Pflüger has ascertained the conditions which must be observed if ammonia or free sulphuric acid has to be determined in presence of ammoniacal salts.

According to the author's experiments the titration is completed in about one hour if about 1 to 10 c.c. of sulphuric acid is present in excess (1 c.c. = 0.001 grm. N), if it has to be determined in about 450 c.c. of liquid, and not more than 1 c.c. of a 20 per cent solution of potassium iodide and 13 c.c. of a 4 per cent solution of potassium iodate are used. The quantity of the ammonium sulphate present may correspond to as much as 50 m.grms. nitrogen. If the total volume of the liquid to be titrated amounts to less than 450 c.c., the end of the titration is reached more rapidly, and after the lapse of an hour the true value will have been exceeded. If the utmost accuracy is required, it is well to make up the liquid always to the same volume, i.e., to 450 c.c.

If the titration is to be executed more rapidly, we add 2 c.c. of solution of potassium iodide and 2.6 c.c. of solution of potassium iodate to 450 c.c. of the liquid to be titrated. The true value is then found in a quarter of an hour.

In order to bring the process at once to a conclusion we take to 450 c.c. of liquid, 3 c.c. potassium iodide and 3.9 c.c. potassium iodate. A larger quantity of the iodine salts should not be used.

Pflüger prefers in general to use minimum quantities of iodine salts, as he has no experience to decide whether in an expedited titration slight differences in the temperature of the laboratory may not occasion greater differences.

Gröger recommends the iodometric method for the determination of acids and bases. He uses a decinormal solution of thiosulphate, a decinormal sulphuric acid, and perfectly neutral solutions of potassium iodide and iodate. The solutions of potassium iodide (24 grms. in 100 c.c.) and iodate (4 grms. in 100 c.c.), are kept separate and before each experiment equal volumes of both solutions are mixed in the quantities required.

In order to ascertain the efficient value of the solution of thiosulphate, Gröger weighs about 0.15 grm. of pure, dry potassium iodate with accuracy, dissolves it in little water, and adds about six times the quantity of potassium iodide. The iodine is liberated by an excess of hydrochloric acid, and the solution of thiosulphate is run in until the liquid is totally decolourised, using starch-paste as indicator. The standard of the decinormal acid is ascertained in the ordinary manner.

In determining free alkalies we supersaturate with a known quantity of decinormal acid and determine the excess of the latter iodometrically, with the addition of 5 c.c. of the solution of potassium iodide and iodate. In this manner Gröger determined most successfully both known quantities of potassa and soda-lye and free ammonia.

If a solution of alkaline carbonate is mixed in the cold with decinormal acid in excess, and at once titrated back after the addition of the iodine salts, the blue colour constantly reappears in the solution which has become colourless. Approximately correct results are obtained if we take into calculation that quantity of thiosulphate which just suffices to keep the liquid colourless for some seconds. This disturbing influence of carbonic acid depends on the fact that it exerts at the same time a decomposing influence upon the iodine salts. To obtain accurate results it is therefore advisable, after adding the excess of decinormal acid, to expel the carbonic acid by ebullition, and then to determine the acid iodometrically in the liquid when completely cold.

* *Zeit. für Angew. Chemie und Zeit. für Analytische Chemie.*

As in the determination of the alkaline carbonates, it is judicious in the determination of the sulphides and hydrosulphides of the alkaline metals to boil the liquid after supersaturation with normal acid. If the expulsion of the sulphuretted hydrogen by boiling is omitted and the liquid supersaturated, the decinormal acid is at once mixed with a sufficiency of the solution of the iodine salts. On the addition of the solution of iodine salts, the sulphuretted hydrogen is decomposed according to the equation: $\text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{S} = 6\text{KI} + 3\text{H}_2\text{O} + \text{S}_3$, and iodine is eliminated corresponding to the excess of acid.

(To be continued).

THE PLAGUE OF FIELD-MICE IN THESSALY SUCCESSFULLY COMBATED BY MEANS OF *BACILLUS TYPHI MURIUM*.

By F. LÖFFLER.

THE author, who has found a new bacteriological method of combating the plague of field-mice by means of *Bacillus typhi murium* (the inciting organism of mouse-typhus), had last spring, in accordance with an invitation from the Greek government, the opportunity to prove his method on the large scale in Thessaly, where field-mice had been multiplying to a frightful extent and threatened to destroy the plentiful harvest of this season.

From the author's interesting report on his activity we learn that the Thessalian field-mouse, rather different in its appearance from our field-mouse (as accurate determination of the species will be given), is even more susceptible to the bacillus of mouse-typhus than our native field-mouse. In addition to these animals no other species seems to be susceptible to the bacillus. Dogs, horses, asses, goats, sheep, like men, are not susceptible to the infection.

The preparation of the nutrient liquid is effected in large 60-litre vessels like milk cans. Into these is put a decoction of straw, mixed with peptone and glucose, neutralised with sodium carbonate, and sterilised by three times boiling for two hours each in a current of steam. After the vessels had cooled down to about 40° they were infected with a pure culture of the bacillus and set aside at above 30°. In the course of two days the bacilli had been developed in the vessels in abundance. On the other hand, water (in portions of one litre each), was infected with pure cultures raised on agar which had congealed in a slanting position. Pieces of bread of the size of a finger-joint were saturated with these liquids rich in bacilli, and the pieces thus impregnated were thrust into the holes of the mice.

Although vegetation was luxuriant, and there seemed no reason why the mice should not prefer their natural food to any artificial substitute, the bread soon disappeared, and in a few days there were found dead mice which displayed the pathological characters of mouse-typhus, and which contained the characteristic bacilli of the disease in their organs. From day to day the result became more decisive, and the representatives of the Greek government gladly admitted the success of the new method.

The hopes that in the bacillus of mouse-typhus we have an effectual remedy against the plague of field-mice, which yearly occasions in all European countries damage amounting to millions, have proved fully justified. For the first time it has been thus found practicable to combat successfully a destructive form of vermin with bacteriological means.—*Centralblatt f. Bakteriologie und Chem. Zeitung*.

Certain Double Salts of Quinine.—E. Grimaux.—The author has obtained and examined the quinine chlorhydrosulphate, bromhydrosulphate, and iodhydrosulphate, and also the quinine chlorbrom- and iod-hydrophosphates. —*Comptes Rendus*, cxy., No. 17.

SUCROSE, DEXTROSE, LEVULOSE:

THEIR QUANTITATIVE DETERMINATION WHEN OCCURRING TOGETHER.*

By F. G. WIECHMANN, Ph.D.

AN accurate method for the determination of sucrose, dextrose, and levulose, when occurring together, has long been sought for in sugar-chemistry, for such a method of analysis would prove valuable for the solution of many questions of interest and importance.

The solving of this problem,—a problem of acknowledged difficulty,† has been attempted by different workers and in various ways.

For some years past it has also engaged the attention of the writer, and in the *School of Mines Quarterly* (vol. xi., No. 3; vol. xii., No. 3), Columbia College, New York, are given some of his former studies on this subject.

The method of analysis there described,—a method based solely on gravimetric determination, yet awaits, in order to furnish results reliable under all circumstances, discovery of some agent whereby the complete destruction of either the dextrose or the levulose may be accomplished, while the sugar not destroyed shall remain entirely unchanged in its properties.

As the chances for immediate success in this direction did not seem very promising, the solution of the tempting problem was sought and found in another manner.

In recording in this paper the successful outcome of his quest, the writer desires to acknowledge his obligations to those who before him have attempted his task, and a critical study of whose labours has proved of value to the writer in his own researches. Furthermore, his sincere thanks are due to his assistant, Mr. E. C. Brainerd, for much valuable work most carefully and conscientiously performed in this investigation.

The method here to be described involves but three simple analytical operations: two gravimetric determinations, and one optical examination with the polariscope. The method is therefore easy and rapid of execution, and at the same time, with careful manipulation, yields most accurate results, as will appear from the various trials to which the method was subjected in order to determine its value and delicacy. A full record of these experiments follows the subjoined description of the method.

The Method.

Preparation of Solution.—If not already in solution, make of the sample to be examined a solution of arbitrary density. Of course, it goes without saying that this method is to be applied only in cases where no other optically active substances are present besides sucrose, dextrose, and levulose, and that care must be exercised that no preliminary treatment of the solution shall influence its original power of rotation.

The specific gravity of the solution above referred to is accurately determined by balance, and from this value there are calculated in the following manner the number of grms. of solution which contain 10,000 grms. of dry substance.‡

Ascertain the degree Brix corresponding to the specific gravity found. Divide 100 by the degree Brix; the quotient represents the number of grms. of solution, which contain 100 grm. of dry substance. This value is multiplied by ten, and the product represents the number of grms. of solution, equivalent to 10,000 grms. of dry substance.

This amount is weighed out, placed in an accurately graduated 100 c.c. flask, and the solution in the flask is made up to 100 c.c. with distilled water.

* From the *School of Mines Quarterly*, xiii., No. 3.

† Thus B. Tollens (*Kurzes Handbuch der Kohlenhydrate*, p. 90):

"Sehr schwierig ist die Bestimmung, wenn Gemenge von Levulose mit anderen Glycosen wie Dextrose oder mit Rohrzucker vorliegen."

‡ This concentration is chosen because the specific rotary powers of the sugars, values needed in the calculation of results, vary with the concentration.

The determinations to be made are as follows:—

Optical Examination.—Some of the solution is placed in a water-jacketed polarisation-tube, a thermometer is inserted in the solution, and a reading on this solution is taken in the polariscope at the temperature of 20° C.

The reading thus obtained must be reduced to the basis of a reading made in a 100 m.m. tube.

Furthermore, if a sugar-polariscope has been used for the observation, the reading obtained must be transformed into circular degrees. With a polariscope using 26.048 grms. as the normal weight, the factor 0.346 is used for the sodium ray.

Gravimetric Determination before Inversion.—Of the 10 per cent solution weigh out an amount equivalent to 1.0 gm. of dry substance. Make this up to 150 c.c., and of this solution take 24.4 c.c., equivalent to 0.1628 gm. dry substance. Take 50 c.c. of Fehling solution,* heat to boiling; while boiling add the 24.4 c.c. of sugar solution and boil for three minutes.

Then remove from flame, add cold distilled water, previously boiled, in order to cool the solution and prevent a further deposition of cuprous oxide.

Filter through a weighed asbestos filter, wash first with boiling water, then with absolute ethyl alcohol, and finally with ether. Dry perfectly, cool and weigh.

Calculate the cuprous oxide to its equivalent of metallic copper, and from the copper thus found ascertain the amount of sucrose corresponding.† From this figure the total reducing-sugars by adding $\frac{1}{2}$ to the sucrose value indicated.

Gravimetric Determination after Inversion.—Of the original 10 per cent solution weigh off an amount equal to 5.000 grms. dry substance; invert with 4 c.c. of concentrated HCl (specific gravity 1.20) by heating on boiling water-bath up to a temperature of 67° C. and maintaining the solution at that temperature for five minutes. Then remove the flask, cool it and its contents to the temperature at which the flask was graduated, and then make the solution up to 100 c.c.

Of the solution thus obtained take 20 c.c. and neutralise with sodium carbonate; then make up to a volume of 150 c.c. with distilled water; of this solution take 24.4 c.c., equivalent to 0.1628 gm. of dry substance, and proceed precisely as previously directed. Determine the value found, as before, from the table; the result obtained represents the total sugars present, expressed as sucrose. From this amount subtract the sucrose value found by prior determination,‡ and the difference represents the amount of sucrose actually present.

The results thus obtained represent the polarisation, in a 10 per cent solution, of the three sugars combined; the total reducing sugars present; the amount of sucrose present.

In cases where the reducing sugars, i.e., the dextrose and the levulose together, exceed in amount the sucrose present, the gravimetric determinations before and after inversion should preferably be made according to E. Meissl's method for the determination of invert sugar (*Zeit. des Vereines für Rübenzucker Industrie*, vol. xxix., p. 1034, and E. Wein *Tabellen zur Quantitativen Bestimmung der Zuckerarten*, Table No. IV.).

Calculation of the Results of Analysis.

This can be accomplished by algebra, or by allegation.

By Algebra.

Let—

a = amount of sucrose present.

b = amount of total reducing sugars present.

* Cupric sulphate cryst., 34.639 grms. in 500 c.c. water; Rochelle salts, 173.000 grms. in 400 c.c. H_2O ; sodic hydrate, 50.000 grms. in 100 c.c. H_2O .

† Table published by the German Government, Law of 1887; also in Wichmann, "Sugar Analysis," Table XI.

‡ That is, the amount as actually found by table prior to the addition of 1-20th.

x = amount of dextrose present.

y = amount of levulose present.

s = the specific rotatory power of sucrose, divided by 100.

d = the specific rotatory power of dextrose, divided by 100.

l = the specific rotatory power of levulose, divided by 100.

p = polarisation observed, expressed in circular degrees.

Then—

$$(as + xd) - yl = p.$$

$$(as + xd) = p + yl.$$

$$xd = p + yl - as.$$

$$x = \frac{p + yl - as}{d}.$$

Substituting this value of x in the equation—

$$x + y = b$$

there results—

$$\frac{p + yl - as}{d} + y = b.$$

$$p + yl - as + yd = bd.$$

$$yl + yd = bd - p + as.$$

$$y(l + d) = bd - p + as.$$

$$y = \frac{bd - p + as}{l + d}.$$

As y represents the amount of levulose, y deducted from b will give at once the amount of dextrose. Or, if preferred, the value of x can also easily be calculated independently.

Example—

Sucrose = a = 8.50.

Total reducing sugars = b = 1.50.

Polarisation, expressed in circular degrees = p = 5.6426.

Specific rotatory power of sucrose $\div$ 100 = s = + 0.665.

Specific rotatory power of dextrose $\div$ 100 = d = + 0.535.

Specific rotatory power of levulose $\div$ 100 = l = - 0.819.

Dextrose present = x .

Levulose present = y .

$$(8.50 \times 0.665 + x \times 0.535) - (y \times 0.819) = 5.6426.$$

$$(8.50 \times 0.665 + x \times 0.535) = 5.6426 + (y \times 0.819).$$

$$0.535x = 5.6426 + 0.819y - 5.6525.$$

$$(1). \quad x = \frac{-0.0099 + 0.819y}{0.535}.$$

$$(2). \quad x + y = 1.50.$$

Substituting the value of x found in equation (1) in equation (2) there results—

$$\frac{-0.0099 + 0.819y}{0.535} + y = 1.50.$$

$$-0.0099 + 0.819y = 0.8025.$$

$$1.354y = 0.8124.$$

$$y = 0.600.$$

Total reducing sugars present. . . . = 1.50

Levulose present = 0.60

Dextrose present = 0.90

By Allegation.

Example—

Determinations made on a 10 per cent solution.

	Per cent.
Sucrose present	= 66.0
Total reducing sugars present	= 34.0
Polarisation observed.	= 2.8199
Polarisation due to the sucrose = 6.6	
$\times 0.665$	= 4.3890

Difference due to the 3.40 per cent reducing sugars = 1.5691

$$\begin{array}{r} 34:100::1'5691:x \\ 156'91 \div 34 = -4'615. \\ +53'5 \quad \quad 35'75 \\ -81'9 \quad \quad -46'15 \\ \hline 99'65 \\ 135'40 \end{array}$$

135'4:35'75::34:x=8'98 per cent of dextrose.
135'4:99'65::34:y=25'02 per cent of levulose.
Or else, having found the percentage of dextrose as above,—

	Per cent.
Total reducing sugars	= 34'00
Dextrose present	= 8'98
Levulose present	= 25'02

As to reporting the nature of the reducing sugars, the analysis of course only warrants the stating of the actual amounts of sucrose, of dextrose, and of levulose as found.

Should it, however, be so desired, equal quantities of dextrose and levulose might be considered as present in the form of invert sugar.

The dextrose or the levulose, of whichever one least is found, might be regarded as combined with an equal amount of the other, forming invert sugar, and any excess over the amount so disposed of could be reported as free or uncombined dextrose, or levulose, as the case might be.

(To be continued).

ON IRON RUST POSSESSING MAGNETIC PROPERTIES.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.
(Concluded from p. 232).

No. 12.—Rust from Cast-Iron Gas Plug-Box.

14'26 grms. were passed through a No. 60 sieve and found to be wholly magnetic.

This rust was in the form of thick scales, strongly magnetic, and when broken open presented in places a crystalline structure. Under the microscope some of the crystals could be recognised as more or less well formed octohedrons of a bluish-black metallic colour and lustre, and they doubtless were crystals of magnetite. The scales of rust were found to have in one case a specific gravity of 4'23 at 15° C.

No. 13.—Rust from Old Gate Hinges.

These had been left lying in an open barrel; the powdered rust was wholly magnetic.

No. 14.—Rust from Sydney Water Mains.

The Sydney water mains choke up very rapidly with "rust," and have in consequence to be replaced from time to time. The deposit consists of hydrated sesquioxide of iron, iron monoxide, silica, alumina, lime, sodium chloride, &c., organic matter, and some free sulphur; the last is derived from the reduction of sulphates by the organic matter.

Fifty grms. of the rust from the interior of some 6-in. mains, kindly supplied to me by Mr. Houghton, gave, when crushed in a porcelain mortar and passed through a No. 60 sieve, 9'33 grms. of magnetic particles.

Fifty grms. from another specimen less finely ground gave 6'79 grms. of magnetic oxide.

A third sample was passed through a No. 90 sieve, and then ground in an agate mortar, but it gave much trouble

from clogging together into cakes. 22'719 grms. of this were washed in a Knop's soil-washing apparatus. Some of this was washed away and lost from its extreme lightness, but the 4'02 grms. of black powder left were entirely magnetic.

No. 15.—Rust from Decayed Gas-Pipes, Melbourne.

Mr. G. Foord, F.C.S., of the Melbourne Mint, examined in 1867 certain gas-pipes which had been almost wholly converted into ferric hydrate. (See "Decay of Gas-Pipes in Certain Soils," G. Foord, *Transactions Royal Society of Victoria*, 1874).

It was found that the gas-pipes near the site of the Melbourne Old Exhibition were subject to very rapid decay. The site is one hundred feet above high water mark of Hobson's Bay. The porous soil of harsh, nearly white, mottled permeable clay is also favourable to drainage by percolation, and described as free from any constituent likely to corrode the pipes unduly.

He found the specific gravity to be—

A.—Undecayed portions.. ..	5'99
B.—Decayed portions	2'57
C.—Portion with thin inner shell of metallic iron	2'88
D.—Grey cast-iron for comparison	7'10

"The decayed portion had lost to some extent, but not altogether, its magnetic properties. It is easily reduced to a greenish brown powder, approaching the tint of raw umber. On solution in hydrochloric acid it evolves no hydrogen, a fact which shows that it contains no residue of iron in the metallic state; when thus dissolved it leaves a bulky residue of graphite, with silicon, carbon, and sulphur compounds of iron and manganese."

"The converted portion when newly taken from the ground is soft, but hardens on exposure."

Further details are given, but the above are sufficient for my present purpose, except that it may be stated that Mr. Foord attributes the rapid oxidation and decay to the action of soluble chlorides in the soil, as has been stated to be the cause in other places.

A piece of the decayed pipe was forwarded by Mr. Foord in 1869 to the late Dr. Smith, Professor of Physics in the Sydney University, who gave it to me some years ago when I was examining some cast-iron which had been acted upon by sea-water. (*Journal Royal Society of New South Wales*, vol. xiv., 1880).

The fragment resembles a curved shell-like piece of limonite. On crushing, it yields an ochre-coloured powder, which is in part attracted by the magnet, but free from particles of metallic iron. Another piece weighing 7'397 grms. yielded a little iron to iodine in potassium iodide, but was still wholly magnetic after the removal of the metallic iron. Other portions did not yield any iron to iodine in potassium iodide.

No. 16.—Rust from Hot-Water Pipe, Prince Alfred Hospital, Sydney. An ordinary 1½-in. pipe.
Of a red-brown colour and feebly magnetic.

No. 17.—Rust from Cold-Water 1½-in. Pipe, Prince Alfred Hospital, Sydney.

Partly magnetic. The non-magnetic portion contains much organic matter.

No. 18.—Rust from Screw and Nail, which had been exposed for a few months on a window sill.

They were both covered with a thin coat of dark brown oxide. The rust from both was attracted by the magnet, but not wholly; the quantity was small, and no attempt was made to weigh or estimate the amount.

19.—Rust from Old Bolt.

A small part of this was non-magnetic, but became feebly attracted after boiling in water.

* From the *Transactions of the Australasian Association for the Advancement of Science*, Hobart Meeting, 1892.

The writer has on various occasions cited the skin of magnetic oxide on meteorites as a proof of the high temperatures to which they have been subjected in their passage through the atmosphere; but in some cases this may perhaps have been found in the ordinary way, inasmuch as the foregoing experiments seem to show very clearly that the oxides yielded by the atmospheric rusting of iron may also be magnetic.

Experiments on the Rusting of Iron.

While the volume has been going through the press I have been able to obtain additional results from certain experiments which were going on when the paper was read, especially those upon sheet iron, nails, &c., which had been placed out to rust or immersed in cylinders of distilled water, &c.

The results do not differ from those already obtained and stated when the paper was read, but the extra time has enabled me to get thicker and heavier deposits of oxide, which are more satisfactory than thin films.

Black sheet iron was scoured with pumice-stone until perfectly bright, clean, and free from scale, and cut into strips 7×2 inches. The strips were then put up into lots of about 1 lb. each.

Experiment No. 1.—A hole was punched in each strip and a bundle of them suspended by a bright iron wire outside a window on September 11, 1891, when they weighed 456 grms. On February 16, 1892, *i.e.*, after nineteen weeks' exposure, these were scraped with a horn spatula and 2.14 grms. of rust obtained, of which only 0.184 grm., or 8.6 per cent, was non-magnetic. The colour of rust was ochrey outside and black inside.

Experiment No. 2.—A second lot of 457 grms. was suspended in the same way on the roof of the chemical laboratory. On February 16, 1892, *i.e.*, after nineteen weeks' exposure, these also were scraped with a horn spatula and yielded 6.6 grms. of rust, of which only 0.775 was non-magnetic, or 11.7 per cent. The rust was of the usual colour outside, but nearly black underneath.

Experiment No. 3.—A third bundle of sheets, weighing 453 grms., was placed in a 24-oz. stoppered cylinder of boiled distilled water on September 11, 1891. This iron was scraped on May 27, 1892, after thirty-six weeks' action, with a horn spatula, and brushed with a new nail-brush, and yielded 2.604 grms. of blackish oxide, of which the whole was attracted by the magnet.

Experiment No. 4.—A further bundle of 453 grms. was placed in a similar stoppered cylinder of unboiled distilled water, treated in the same way as Nos. 2 and 3, and on the same dates. Yielded 0.694 grm. of dark brown oxide, wholly lifted by the magnet.

Experiment No. 5.—453 grms. of strips were similarly placed in a cylinder of tap water on May 27. They were taken out, dried on a water bath, scraped with a horn spatula, and carefully brushed; the rust weighed 0.538 grm.; it was of a dark brown colour and wholly attracted.

Experiment No. 6.—A bundle of strips, weighing 449 grms., was placed in cylinder of distilled water charged with carbon dioxide. Treated in the same way as the others and on the same dates. This yielded 0.545 grm. of a dark yellowish brown colour. Some of the oxide in this case was in the form of brown iridescent films floating in the water. These brown films were also found to be magnetic after boiling; they were also found to yield no blue colouration with potassium ferricyanide added to their solution in hydrochloric acid. In all the other cases (1 to 5) the loose oxide floating in the water and attached to the iron was black.

Experiment No. 8.—453 grms. of bright 2 in. wire nails were exposed in a photographic dish on a window sill from September 11, 1891, to February 16, 1892. These nails were moistened from time to time, but not kept constantly wet. On scraping off the rust with a horn spatula, 7.79 grms. of rust were obtained, the whole of which was magnetic.

Experiment No. 9.—453 grms. of 6-in. bright wire nails were similarly exposed and treated at the same time. These nails only yielded 4.03 grms. of rust, which was also wholly magnetic. The smaller surface exposed by the larger nails accounts for the smaller weight of rust produced.

Experiment No. 10.—On September 21, 1891, 906 grms. of bright 6-in. wire nails were put out on a window sill (facing W.) in a new photographic dish, and covered with distilled water. After three days, *i.e.*, on the 24th, they were covered with loose ochrey rust which washed off readily, but under this and filling the striæ of the nails was a film of black oxide. When scraped on February 16, 1892, with a horn spatula, they yielded 4.03 grms. of rust of a dark brown colour, and entirely attracted by the magnet.

Experiment No. 11.—At the same time and place 1½ lbs. of bright 2½-in. wire nails were also put out in a photographic dish with the same result, except that there was very much more of the black oxide present.

On turning over the nails Nos. 10 and 11 on the 26th, *i.e.*, after five days' exposure, it was found that, while covered more or less completely with ochrey rust on the upper surface, the lower surfaces of the nails (which were completely immersed in the water) were free from it, but coated instead with a closely adherent film of black oxide, due apparently to the fact that, while there was sufficient oxygen on the exposed side of the nails to form both the red or ochrey and black oxide on the lower side (completely immersed in water) the oxidation did not go beyond the first stage. On February 16, 7.79 grms. of entirely magnetic rust were obtained.

The total amount of rust furnished by this experiment and No. 10 was much more than the weights given. The loose rust in the dishes was not weighed, because it was mixed with grit and dust which had fallen into the dishes during their exposure.

Experiment No. 12.—Some sheets of clean iron were also placed out, but not moistened. The rust was much darker in colour than that from Experiments 10 and 11, being of a dark reddish brown when scraped off with a horn spatula and powdered. The oxide weighed 2.14 grms., of which 0.184 was non-magnetic.

Experiment No. 13.—On September 21, 1891, 736 grms. of bright 6-in. wire nails were placed in a stoppered cylinder of hot and freshly boiled distilled water. In the course of a day or two they were coated with black oxide. On May 31 the oxide was collected, but only amounted 0.131 grm., which was feebly magnetic.

Experiment No. 14.—702 grms. of bright 6-in. wire nails were put up with distilled water charged with carbon dioxide. Gave only 0.211 of rust, of which but a small part was magnetic.

Experiment No. 15.—On September 22, 1891, 433.5 grms. of bright wire nails were placed in a stoppered cylinder, and dry ozonised oxygen from a Siemens tube passed in for twenty minutes. These nails were hardly rusted, and there was insufficient rust to remove.

Experiment No. 16.—415.3 grms. were also put up in the same way, and moist ozone passed in for about twenty minutes. Yielded on May 31, 1892, 1.437 grms. of highly magnetic oxide.

The absence of metallic iron was in these cases proved by grinding it in agate mortar, and in certain cases also by means of iodine.

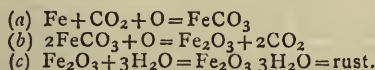
Literature.

Although the results of previous investigators should usually have precedence, they are given at a later stage of this paper mainly because most of my experiments were carried out before I had time to fully look up the literature of the subject. The immense number of publications and amount of matter to be gone through nowadays is so overwhelming that if, in all cases, the necessary searches were to be made before experimenting, many questions which crop up would never reach the experimental stage at all.

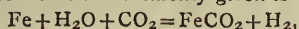
In the first instance I had, from want of time, to be content with reference to the chemical dictionaries and other standard works on chemistry, and as they were silent upon this subject, or stated that there was only one oxide of iron possessing magnetic properties, I went on with the experiments, and they were practically finished before I was able to go through the journals devoted to chemistry and allied subjects.

From the quotations which follow it will be seen that the views of the older chemists more closely correspond with my results than those of some of the more recent writers.

Most modern writers state that rust is non-magnetic, and is formed only in the presence of air, moisture, and carbon dioxide as follows:—



This of course may more or less explain the reactions, but it evidently is too neat and complete, inasmuch as it does not account for the large proportion of magnetic oxide which always appears to be present in ordinary rust. Another reaction commonly given is—



and that the FeCO_3 formed takes up more CO_2 and is converted into the soluble acid carbonate, which in turn is converted into the insoluble ferric hydrate ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) or rust, and that the CO_2 is free to act again, but this is equally imperfect. Mendeleeff ("Principles of Chemistry," London, 1891, p. 321), amongst modern writers, recognises the fact that rust contains both ferrous and ferric oxides, but makes no mention of its magnetic properties.

In looking up the matter reference was first made to the later publications, but it was only in those published over thirty years ago that anything was met with really bearing upon the subject, the most interesting and valuable being the note by Mr. Robbins in the *CHEMICAL NEWS* for 1859, and the paper by M. Sarzeau in 1860, also in the *CHEMICAL NEWS*; both of these, however, seemed to have been ignored or overlooked by late writers.

The following quotations are arranged according to their dates of publication:—

It is stated in the "Dictionary of Chemistry and Mineralogy," by A. and C. R. Aiken, 1807, on p. 612, that "The common rust which collects upon hammered iron by exposure to air and moisture, and which in time corrodes the thickest bars, is not the simple oxyd, but a carbonated oxyd, or a compound of iron, oxygen, carbonic acid, and water, and is not of itself magnetic, unless mixed with fragments of iron detached by the rusting."

It is stated, too, that iron will oxidise and hydrogen be given off "even at the common temperature of the air, but the oxyd will then be in the form of a black powder, and will not exhibit that glossy appearance which it does in the former method," i.e., when steam is passed over red-hot iron. "The preparation called martial æthiops is iron oxidated by water, and was first made by Lemery the younger" by covering a quantity of clean iron filings with water, and stirring from time to time. "After a while bubbles of hydrogen constantly rise from the mass, and the vessel becomes full of a very fine black powder. This black powder is iron in the first or lowest state of oxidation or sub-oxyd; it is strongly magnetic, but has a constant tendency to absorb an additional quantity of oxygen from the air or any other substance by which it loses its magnetic property, changes from black to yellow or red, and acquires very different chemical characters."

Further, "Von Mons, having prepared a quantity of this black sub-oxyd, heated it in a retort to drive off the superfluous moisture, but on taking it out "a spontaneous motion or heaving took place through the mass; it became so hot as to burn a thick double paper in contact with it, and the whole in a few minutes was converted into the red or perfect oxyd or saffron of Mars."

Leopold Gmelin, in his "Handbook of Chemistry," vol. v., p. 185, Cavendish Society, 1851, says:—"Iron covered by a thin layer of water and exposed to the air is converted into the hydrated sesquioxide; ammonia is also formed."

"If the iron be covered by a deeper stratum of water so that the transference of the oxygen of the air through the water to the iron may take place more slowly, a formation of black hydrated ferroso-ferric oxide takes place, because hydrated ferric oxide, as it slowly forms, induces the iron to decompose the water and form ferrous oxide, with which the ferric oxide then unites.—(Wöhler)."

Page 186: "Beneath the flocculent hydrated sesquioxide of iron there is formed a thin black crust (of ferroso-ferric oxide?) which adheres firmly to the iron."

"When cast-iron of this description (i.e., mixed grey and white) is exposed to the action of a mixture of seventy-five measures of aerated water and one measure of a saturated solution of chloride of sodium and carbonate of sodium, oxidation begins in a minute, and thus is formed—first, whitish hydrated ferrous oxide and hydrated ferroso-ferric oxide, which at some distance from the iron are converted into hydrated ferric oxide, and afterwards carbonate and silicate of ferrous oxide, the latter being produced by the oxidation of silicide of iron."

Page 186: 6. "At ordinary temperatures, and out of contact of air, iron does not decompose thoroughly boiled water, unless it is in contact with more electro-negative bodies, as with previously formed ferric oxide, mercury, &c. In this case, and likewise when the liquid is heated to 50° or 60°, a feeble evolution of hydrogen takes place, and ferroso-ferric oxide appears to be formed.—Hall, 2 *J. C. S.*, vol. vii., p. 55. Guibourt, *Ann. Chim. Phys.*, vol. xi., p. 43).

Page 187: "Ferrous oxide decomposes water by continued contact, and is converted into ferroso ferric oxide."

Page 188: "If a ferrous salt be precipitated by ammonia instead of by potash, the precipitate, after long standing, gives off hydrogen gas, becomes gradually darker in colour, and when dried in the manner above described is converted into black ferroso-ferric oxide containing ammonia.—(G. Schmidt, *Ann. Pharm.*, xxxvi., 101).

"Dried ferrous hydrate is not magnetic (Liebig and Wöhler), and on exposure to the air it is instantly converted into ferric oxide. The heat often rises to redness."

Page 193: "Iron black or *Æthiops Martialis Lemeryi* is a mixture of ferric and ferrous oxides in different proportions, according to the mode of preparation, and is partly hydrated."

Page 194: "Hydrated *Æthiops*.—Iron filings are placed in a wide vessel covered with a deep stratum of water, exposed to the air for a considerable time with frequent stirring, the light black powder is decanted from the still unoxidised iron from time to time, collected on a filter, and rapidly dried. This preparation is doubtless identical with the black hydrate of ferroso-ferric oxide already described."

The above quotations are given because they give a more accurate account of the process of the oxidation of iron than some of the more modern writers.

J. Robbins, in a note on "Magnetic Peroxide of Iron," *CHEMICAL NEWS*, vol. i., 1859, p. 11, states that he ignited some black magnetic oxide of iron on platinum foil over a spirit lamp. "After ignition the black oxide had apparently become converted into the common red peroxide of iron, but on applying the magnet, to my great astonishment I found that its magnetic properties remained unimpaired. The next question to determine was whether it was still a combination of the two oxides having undergone some molecular change, or whether the protoxide had not become converted into peroxide by absorption of oxygen from the atmosphere. I therefore dissolved some of the red powder in hydrochloric acid, and to the solution added some ferridcyanide of potassium, but not a

trace of the protosalt was indicated by that reagent. The magnetic peroxide may also be conveniently prepared by fusing together for some minutes the common black oxide with three or four times its weight of nitrate of potash. Prepared in this way it is more readily dissolved by hydrochloric acid than that obtained by simple ignition.

"I have searched various chemical works, but can find no mention of a magnetic peroxide of iron. I therefore presume that this peculiar compound has escaped observation."

M. Sarzeau (*CHEMICAL NEWS*, i., 1860, p. 137, and *Journ. de Pharm. et Chimie*, Jan. 23, 1860), in describing a method of preparing aerated water from plates of iron placed in a solution of carbonic acid in water at 50° F., says:—"We obtain a liquid with well-marked inky flavour, and which has all the properties of a solution of a protosalt of iron. If the liquid be heated it is at first turbid, and then becomes milky, afterwards ochrey, and at last when it boils it suddenly changes to a deep brown. On cooling it deposits a substance of the same colour, which, separated by filtration, dried in the air, and dissolved in hydrochloric acid, gives a mixture of protochloride and perchloride of iron. If a magnet be brought in contact with the brown matter when dry it is found to adhere, showing that by heating a solution of carbonate of iron magnetic oxide is formed."

I did not come across the accounts of the experiments by Mr. Robbins and M. Sarzeau until my own were practically completed, as they are not quoted in any of the Chemical Dictionaries and works of reference, but I have since repeated them, and can confirm their results.

Robbins's experiment of heating finely-powdered magnetite was repeated on several samples of magnetite, and in each case the resulting sesquioxide of iron was found to be wholly attracted by a magnet, although no trace of ferrous oxide could be detected in the red powder by dissolving in hydrochloric acid and adding potassium ferricyanide.

The powder is still attracted by the magnet when hot, but more strongly on cooling, as in the case of metallic iron.

M. Sarzeau's results were confirmed by converting precipitated ferrous carbonate into the acid soluble carbonate by passing carbon dioxide through water containing ferrous carbonate in suspension. On warming this solution or exposing it to the air the carbon dioxide escaped, and a dark-coloured precipitate was thrown down. Usually this was found to be attracted by the magnet, but not always. On further warming and longer exposure it gradually acquires a buff colour and becomes magnetic, although not strongly so, but seen by adding upon it with the magnet under water. A temperature of about 70° C. seemed to be the best. At from 270° to 290° C. the colour became red, the magnetic properties being retained even after ignition; the solution in hydrochloric acid showed no trace of ferrous salt with potassium ferricyanide.

There is sometimes a little difficulty in obtaining the magnetic sesquioxide by this process. The cause is not quite clear, but is probably due to the ferrous carbonate not having in all cases been thoroughly washed free from other salts.

Dr. F. Crace Calvert, in a paper on the "Oxidation of Iron" (*Journ. Chem. Soc.*, 1871, p. 198, and *CHEMICAL NEWS*, 1871, vol. xxiii., p. 98), gives the following analysis of rust:—

	Conway Bridge, Llangollen.	
"Iron sesquioxide	93'094	92'900
Iron protoxide	5'810	6'177
Iron carbonate	0'900	0'617
Silica	0'196	0'121
Ammonia	—	—
Calcium carbonate	—	0'295 "

No remark is made as to whether the rust was magnetic or not, although it probably was; and the same remark

doubtless applies equally to the rust described by Mr. Cowper and Dr. F. Muck, as follows:—

"Oxidised Iron from the condenser of H.M.S. *Spartan*," by Richard Cowper, A.R.S.M. (*Journ. Chem. Soc.*, 1882, vol. li., p. 256.)

The specimen was found in part of the tank of a surface condenser, and which in use had been constantly subjected to the action of sea-water at a temperature not exceeding 100° F.

It consisted of a brownish substance, in which were embedded numerous shining black particles, and resembled very much in appearance a piece of rusty grey pig-iron. Sp. gr., 2·63 only, and extremely friable. A full analysis is given; there was 42·33 per cent of ferrous oxide and 2·21 per cent of ferric oxide present.

He states also that a specimen of ordinary iron rust scraped from some cast-iron (which had rusted in moist air) gave 65·42 per cent ferric and 7·42 per cent of ferrous oxide.

Dr. F. Muck (*Stahl und Eisen*, viii., p. 837—41, also *Journal Iron and Steel Institute*, 1889, i., p. 385), states that the rust in a boiler formed in pits near the feed-pipe had a fungoid form, and dried at 100° C.; it had the following composition:—

Fe ₂ O ₃	66·84
FeO	23·24
CaO	2·60
MgO	0·39
SiO ₂	1·18
SO ₃	0·28
CO ₂	2·32
C	0·22
H ₂ O	2·75
Organic	0·18

The organic matter was soluble in ether, and probably derived from the lubricants used. "The rust therefore mainly consists of magnetic oxide."

Prof. W. Spring (*Bull. Soc. Chim.*, vol. i., pp. 215—18, and *Journ. Soc. Chem. Industry*, Nov. 30, 1888), says that the cause of iron rails rusting less rapidly when in use than when not subjected to traffic is not due to the vibration of passing trains, nor to currents of electricity, nor to a film of grease derived from the engine and carriages, but rather to the formation of a layer of magnetic oxide on their upper surface formed by the pressure of the wheels on the moist ferric oxide with which they naturally become coated. He mixed damp ferric hydrate with minute particles of metallic iron, and subjected the mixture to a pressure of 1000 to 1200 atmospheres, and found that the two adhered, and that the hydrate became black to the depth of 0·5 m.m. Analysis showed that magnetic oxide had been formed. He also found that the rust taken from a rail contained some magnetic oxide and a little free iron mixed with the ferric oxide, and came to the conclusion that rails in use are protected by the magnetic oxide thus formed by the pressure, just as in the case of iron artificially coated with magnetic oxide.

From the foregoing experiments, and those detailed in a note upon the "Occurrence of Magnetite in Certain Minerals and Rocks," it appears:—

1. That native sesquioxide of iron and its hydrates, such as hæmatite, goëthite, limonite, &c., are themselves non-magnetic, i.e. to an ordinary bar magnet, but may contain some magnetite.

2. That sesquioxide of iron obtained by precipitation from the acid carbonate of iron, and probably from other salts of iron, is magnetic, or may be rendered magnetic by long boiling or by heating at various temperatures up to redness, and that such magnetic sesquioxide is free from any monoxide.

3. That magnetic sesquioxide of iron free from monoxide can be obtained by heating the magnetic oxide, as first shown by Robbins.

4. That ordinary rust produced by the oxidation of metallic iron is usually magnetic, and often polar. Magnetic rust usually contains more or less ferrous oxide, and may accordingly be regarded as $x\text{FeO}$, $y\text{Fe}_2\text{O}_3$, i.e., varying mixtures of FeO and Fe_2O_3 , and of their hydrates, being well known to possess magnetic properties, although in other cases the rust may be quite free from monoxide and yet be magnetic.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 28th, 1892.

Dr. J. H. GLADSTONE, F.R.S., Past President, in the Chair.

Mr. G. H. WYATT was elected a member of the Society.

The Discussion on Mr. Williams's paper "*On the Relation of the Dimensions of Physical Quantities to Directions in Space*," was opened by Prof. PERRY reading a communication from Prof. FITZGERALD, President.

The writer said Mr. Williams disagreed with the suggestion that electric and magnetic inductive capacity are quantities of the same kind, principally because he had not got over the curious prejudice that potential and kinetic energy are different. No theory of the ether could be complete unless it reduced its energy to the kinetic form. Electric and magnetic inductive capacity would probably be found to be similar in the ether and ultimately have the same dimensions. The analogies were not yet complete, but only in respect of matter was it probable that any difference existed between them. Diamagnetism corresponded to electrostatic induction, but paramagnetism had no definite electrical analogue. He was inclined to regard the phenomena of paramagnetism as connected with the arrangement of the material molecules, whilst diamagnetism depended on the electric charges on those molecules. So far no matter had been found which conducts magnetism, and such may not exist in our universe, but it may be gravitationally repelled by matter as we know it.

Mr. MADAN remarked that in the first part of his paper Mr. Williams recognised that dimensional formulæ were originally change ratios, but puts this aside for the higher conception which regards these formulæ as expressing the nature of the quantity. Fourier showed how to find the dimensions of units by making the size of the fundamental units vary; but k (specific inductive capacity) did not vary with the fundamental units, for it was merely the ratio of the capacities of two condensers, and therefore, by Mr. Williams's definition, a pure number. It was difficult, he said, to see how k could have dimensions, but Mr. Williams regarded it as a physical quantity, and therefore possessing dimensions. The object in giving dimensions to k and μ seemed to be to get over the double system of units.

Mr. Madan did not think that dimensions could express the nature of physical quantities, and said differences of opinion existed amongst authorities on this point. For example, Dr. J. Hopkinson at the last British Association meeting said that because a coefficient of self-induction had the dimensions of length it must be a length, whilst other learned professors objected to this view. Even if one admitted that dimensions are a test of the nature of physical quantities, it was not necessary that the two systems of units should be identical. The connecting link between the two systems was $Q = Ct$, and the validity of this equation had been questioned. If this objection be confirmed, then there would be no current in electrostatics, and no Q in the electromagnetic system, and the units would not clash.

Referring to dynamical units, Mr. Madan pointed out that two units of mass were used in astronomy, but astronomers got over the difficulty by using a coefficient. Dimensional formulæ, he said, are the result of a convention that certain definitions should hold true generally, but they contain no further information respecting the nature of the quantities beyond that involved in those definitions. As an example of the inability of such formulæ to express the nature of quantities, he pointed out that whilst physical differences were known to exist between + and - electricity, the dimensional formulæ showed no signs of such differences.

Prof. RÜCKER said every correct physical equation consisted of a numerical relation between physical quantities of the same kind, and might be written either as a mere numerical equation or as a relation between the physical quantities themselves. The equation $2 + 1 = 3$ may correspond to 2 feet + 1 foot = 3 feet, and the latter may be written $2[L] + 1[L] = 3[L]$, where $[L]$ represents the unit of length. So far as he was aware, nobody but a recent writer in *The Electrician* had denied that in such an equation $[L]$ represented a concrete quantity. Maxwell explicitly stated that it does in his article on "Dimensions" (*Encycl. Britt.*) and elsewhere, and Prof. J. Thomson in his paper on the same subject makes no statement contrary to this. The above equation might also be written $2[\text{feet}] + 1[\text{foot}] = 1[\text{yard}]$. Another equation, involving time, is $60[\text{secs.}] = 1[\text{minute}]$, and dividing one by the other one gets—

$$\frac{2}{60} \left[\frac{\text{foot}}{\text{sec.}} \right] + \frac{1}{60} \left[\frac{\text{foot}}{\text{sec.}} \right] = 1 \left[\frac{\text{yard}}{\text{min.}} \right].$$

A difficulty was felt here in understanding what dividing a foot by a second meant; but this difficulty, Prof. Rucker considered, was not greater than that involved in dividing an impossible by a real quantity—a very familiar analytical device. Reasons for regarding the symbols $\left[\frac{\text{foot}}{\text{sec.}} \right]$ as legitimate were then given.

Prof. HENRICI said the communication under discussion was one of the most important contributions to physical science which he had come across for a long time. Such difficulties as presented themselves in the paper arose from its fundamental character. The author had attempted to express all physical quantities in terms of three, but quantities may exist which cannot be completely represented in terms of L , M , and T . The tendency of modern mathematics was to express everything dynamically. Mathematicians had long been in the habit of using quantities which were neither numbers nor concretes in the ordinary sense, and different kinds of algebra, with units not understandable, had been developed. If a quantity a times a unit u , be multiplied by b times another unit, v , the result is expressed by $ab \cdot uv$; where ab is a number, and uv a new unit, which may or may not be physically interpretable. The interpretation of a product depended on the meaning attached to "multiplication," and if this be restricted to "repeated addition" the range is very limited. The narrow conceptions concerning multiplication acquired at school could only be removed by a careful study of vectors. Mr. Williams had treated his subject by vector methods, but a few traces of quaternions remained which might be omitted. To truly understand the subject, vectors must be treated vectorially; dimensions might then show the nature of the quantities involved. The system adopted in Mr. Williams's paper was probably the best attainable at present, but he (Prof. Henrici) looked forward to the use of a more fundamental quantity than the vector—viz., "the point"—as the ultimate basis. Grassmann had worked out a "point calculus" in 1844 which was republished in 1880. Quantities more complex than vectors, viz., rotors, screws, motors, &c., had been used with advantage by Clifford, Ball, and others.

Dr. SUMPNER thought the first ideas of students on the

subject of dimensions were that they represented the nature of the quantities, but could not see why every quantity should be expressed in terms of L, M, and T. Prof. Rücker's paper on "Suppressed Dimensions" had cleared up several important points, and he (Dr. Sumpner) now considered that every quantity must be expressed in terms of a unit of the same kind as itself. He viewed Mr. Williams's attempt to express everything in terms of L, M, and T as rather a retrograde step.

The discussion on Mr. Williams's paper was adjourned, and

Dr. YOUNG made some remarks on Mr. SUTHERLAND'S communication "*On the Laws of Molecular Force.*"

Mr. Sutherland, he said, thought that Ramsay and Young's law, $\delta p / \delta T = f(v)$, is not correct for compounds in the liquid state. Barus, however, has proved that several liquids, including ether, only showed variations from the law at extremely high pressure. After writing the equation of the virial in the form $p v = RT \psi(v) + v \phi(v)$; where $v \phi(v)$ stands for the internal virial term. The author of the paper had shown that $v \phi(v)$ ought to be constant, but finding it not constant in the case of ether, &c., he attempted to explain the discrepancies by the formation of pairs of molecules at small volumes. Other substances, such as nitrogen and methane, were supposed to follow the law. This, Dr. Young said, could not be accepted as proved, for the range of volumes over which the experiments had been made was only small, and methane was difficult to prepare pure. After criticising the use of two and sometimes three "characteristic equations" for the same substance, he went on to show that the formulæ given in the paper by which the critical temperatures, pressures, and volumes might be calculated, lead to results differing from experimental numbers by quantities greatly in excess of experimental errors. Experiment also showed that capillarity had little or no effect on the determination of critical constants. Speaking of critical volumes, he pointed out that MM. Calletet and Mathias had published a method of finding critical densities which gave very accurate results.

Mr. Sutherland's conclusions respecting Van der Waal's generalisations were practically identical with those expressed by Dr. Young in his paper on the subject read before the Society last year. The views as to the nature of the various kinds of "pairing" mentioned in Mr. Sutherland's paper were open to various objections, for his "physical pairing is supposed to produce more effect on the "characteristic equation" than true chemical pairing. In his (Dr. Young's) opinion, the idea of physical pairing appears somewhat speculative, and requires further elucidation.

A paper "*On the Determination of the Critical Density,*" by Dr. YOUNG and Mr. G. L. THOMAS, B.Sc.; and two papers "*On the Determination of Critical Volume,*" and "*On the Boiling-points of Different Liquids at Equal Pressures,*" by Dr. YOUNG, were taken as read.

The first paper gives an account of results obtained by Cailletet and Mathias's method, based on the fact that the means of the densities of a substance in the states of liquid and saturated vapour when plotted with temperature lie on a straight line which passes through the critical point.

In the paper on "Critical Volumes," the above-mentioned method is again referred to, and results obtained thereby accepted in preference to those given by the author in his paper on "Generalisations of Van der Waals, &c.," read before the Society about a year ago. The alcohols do not strictly follow the straight line law. Revised tables of critical volumes, densities, pressures, and temperatures are given, and it is pointed out that for many substances the ratio of the actual critical density to the theoretical density (for a perfect gas) is about 3.8.

The paper on "Boiling-points of Different Liquids at Equal Pressures" contains a comparison of the accuracies with which a formula for the relation between the boiling points given by M. Colst (*Compt. Rend.*, cxiv., p. 653) and

one by Ramsay and Young (*Phil. Mag.*, Jan., 1886) accord with experimental results. The author concludes that the latter formula shows the best agreement, but that of M. Colst is satisfactory under certain conditions.

The further discussion of Mr. Williams's and Mr. Sutherland's papers was adjourned till the next meeting.

NOTICES OF BOOKS.

Commercial Organic Analysis; A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c. With Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S., Past President of the Society of Public Analysts, Public Analyst for the West Riding of Yorkshire, the Northern Division of Derbyshire, the County Borough of Sheffield, &c. Second Edition, Revised and Enlarged. Volume III., Part II., *Amines and Ammonium Bases, Hydrazines, Bases from Tar, Vegetable Alkaloids.* London: J. and A. Churchill, 1892, pp. 584.

This volume, so long expected, will be eagerly welcomed by the chemical public of all English-speaking countries. All readers acquainted with the earlier edition will know that the author has not—as does Fresenius for mineral matters—confined himself to the most approved methods for the recognition and determination of organic chemical individuals. The nature of his subject obliges him to deal not only with compounds but with mixtures, natural or artificial, and in the latter case often fraudulent. Hence much pharmacological matter has been of necessity introduced. The result as a whole must be pronounced exceedingly useful.

The most valuable and important section of the volume before us is that which discusses the vegetable alkaloids so interesting therapeutically, dietetically, and toxicologically. Here Mr. Allen, in addition to his own researches, has collected all trustworthy results up to the present date, and has given us a survey of this class of bodies, hitherto unequalled in our literature.

In these days, when the infectious mania known as anti-vivisectionism is experiencing a recrudescence, it may not be amiss to ask how, in the absence of experiments upon animals could the detection of the poisonous alkaloids ever have been studied? Some of the most dangerous, such as aconitine, cannot be certainly recognised by any chemical test. It is not improbable that secret poisoning may revive in this country owing to the increased difficulties thrown in the way of detection, no less than to the discovery of the toxic action of the ptomaines.

We are commonly told that cocoa, chocolate, or other preparations of the nuts of *Theobroma cacao*, if only honestly made, have a very high nutritive value. But several authorities here quoted show that of the total nitrogen present a very considerable part occurs in the forms of theobromine, ammonia (!), amido-compounds, and other indigestible nitrogenous substances; so that from 30 to 40 per cent of the total nitrogen is not in an assimilable state. For the details, and for the names of the authorities cited, we must refer to the work before us.

The frauds committed upon the public in the sale of coffee and tea are now much less rampant than formerly. But far too much remains. It is a humiliating fact that whilst we pass Acts concerning the sale of food and drugs, and appoint public analysts, we actually grant patents for new methods of adulteration, or rather for making up rubbish into the shape of coffee-beans.

Some reference is made by Mr. Allen to such patents. But so long as the libel laws—"the shield and the sword of the quack and the swindler"—remain rampant, it is impossible to speak truthfully of such proceedings.

One important step would be an enactment that if any substance is made or vended as an addition to coffee or tea, or if the words coffee or tea are used in its name or description, it shall fall within the scope of the Sale of Food and Drugs Act. At present such compositions as "French Coffee," "Coffee as in France," &c., pass free!

Fraudulent coffee-beans are not unknown in Germany, where they are sold as Kunst-Kaffee, Domkaffee, Allerweltkaffee, Mogdad Kaffee, &c. But in that country they do not enjoy the protection of patents.

The absolute identity of theine and caffeine, though generally assumed, is here spoken of as not established beyond doubt.

In treating of the toxicology of opium and its allies, the author exposes some of the exaggerations of the "anti-opiumists." These denounced drugs seem to be almost a necessity of life in malarious districts, not merely in India and China, but in the fenny parts of England. The agitator would do well to note the quantity of laudanum made up and sold every market-day at Horn-castle. It is interesting to observe that so-called "paregoric" is now sold by costermongers! The author remarks that these concoctions, if harmless in themselves, accustom ignorant persons to deal with preparations of opium, and if by any chance genuine paregoric falls into their hands, there is no small danger of an overdose. But the costermonger is, perhaps, as well qualified to dispense poisonous medicines as the draper or the grocer.

The permanence of strychnine in dead bodies even for years is emphasized,—a subject which reminds us of one of the least satisfactory features of the Palmer case.

Strychnine is pronounced, on the authority of Dr. Müller, of Yackandandah, Victoria, to be a good antidote in snake-bite. Among one hundred cases thus treated hypodermically all save one recovered. The species of snake is not mentioned. The question is, would it prove successful against the poison of the cobra?

We can only say, in concluding our brief notice of this admirable work, that it will be found necessary in every laboratory.

Metal Colouring and Bronzing. By ARTHUR H. HIORNS, Principal, Metallurgy and Engineering Department, Birmingham Municipal Technical School. London and New York: Macmillan and Co., 1892. 8vo., pp. 336.

It is exceedingly satisfactory to perceive that a number of technical manuals are now making their appearance which are not mere compilations of recipes strung together at hap-hazard by a compiler innocent of practical knowledge. Mr. Hiorns, on the contrary, though he has diligently collected information on his subject from all available sources, has submitted all recipes obtained to a careful experimental investigation with which he and his colleagues have been engaged for eighteen months. In his preface he calls attention to the nicety of the conditions on which success or failure may turn. The manipulation may in some cases be defective as well as the reagent. Though not exactly in the same words, he recommends his pupils and readers to "mix their colours with brains."

The work emanates from the Birmingham Municipal Technical School,—a most praiseworthy Institution. It appears that the art of producing beautiful colours on metal work had formerly one of its chief centres in Birmingham. It is now, we regret to see, spoken of as an "almost lost art," and we most heartily sympathise with the attempt of the Committee of the School and with Mr. Hiorns not merely to bring it back but to elevate and extend it.

We find with pleasure that the author duly regards

metal colouring as a chemical art, which, if it is to rise above "rule of thumb," pre-supposes a knowledge of chemical principles. These principles, together with the preliminary treatment of metallic objects, form the subject of the first two parts. The remainder of the work is devoted to the three main kinds of colouring, viz., chemical metal colouring, electro-chemical metal colouring, and mechanical metal colouring. For his instructions we must refer the reader to the work itself, expressing our hope that Mr. Hiorns' labours may be duly appreciated and may contribute towards the truly patriotic object which he has in view.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 17, October 24, 1892.

New Researches on the Fixation of Atmospheric Nitrogen by Microbia.—M. Berthelot.—The author's experiments show that no fixation of atmospheric nitrogen by the mere fact of a purely chemical oxidation of the humic acid is effected by the simultaneous action of air and light. But the humic acid serves as a necessary support for the microbia, and in its absence they cannot effect the fixation of the nitrogen.

Protection from Rabies.—The Perpetual Secretary communicated a letter from the French Association for the Advancement of Science in which two prizes of 400 and 200 francs respectively are offered for the best study of the following question: The frequency of rabies and the prophylactic measures in force in any one department (except La Seine), or in a region of two or three departments in France and Algeria. The statistics must extend over at least ten years, and must include the results of 1892.

The Dissociation of Chrome Alum.—H. Baubigny and E. Péchard.—The dissociation of numerous saline compounds on solution is now a well-established fact. At times the formation of a less soluble compound, e.g., a sub-salt or a change of colour, render the occurrence of such a dissociation perceptible. Often it is more difficult to characterise. Graham, by availing himself of the different rates of the diffusion of potassium sulphate and aluminium sulphate, has been able to demonstrate this fact in the case of ordinary alum. On placing a solution of this salt at the bottom of a vessel full of water, he observed, after some time, on analysing the upper stratum of liquid, that the weights of the two sulphates did not co-exist in the proportions corresponding to the production of alum. But as everything becomes equalised in course of time, the phenomenon of dissociation can be studied by this procedure only in the first portion of time. This fact of dissociation may be demonstrated in the chrome-alums in a more distinct manner. Having remarked that ordinary chrome-alum, after being repeatedly precipitated from its aqueous solutions by means of alcohol, always presented an acid reaction, we added to 20 c.c. of a saturated solution 300 m.grms. of ammoniacal gas; after stirring, it was neutral to methyl-orange. Some time afterwards the solution, which had taken a green colour on the addition of ammonia, deposited violet crystals of a distinctly acid reaction, and the mother liquors also became again acid to methyl-orange. This fact can only depend on a partial decomposition of the salt, corresponding to such a state of equilibrium that the liquid is finally acid. This peculiarity is due to the chromium sulphate, for on repeating the experiment with this simple sulphate we found with this compound a

perfectly analogous phenomenon. Ordinary alum and aluminium sulphate do not display the same property. Their solutions, if neutral to methyl-orange, remain at the end of eight days.

Temperature of the Maximum Density of Aqueous Solutions.—L. de Coppel.—There exists an interesting relation between the fall of the congelation-point (C) and the fall of the temperature of maximum density (D). All the substances hitherto studied (except alcohol, and possibly sulphuric acid), are divisible into three groups with reference to the value of the proportion $\frac{D}{C}$. The first group consists of substances which reduce the temperature of the maximum density of water about four times more than they reduce its congelation-point. This group comprises at present caustic potassa, oxalic acid, sodium, potassium and calcium chlorides, and potassium iodide. A second group comprises substances which, like sugar and the alkaline carbonates and sulphates, lower the temperature of the maximum density seven or eight times more than the temperature of congelation. In the third group, which at present is represented only by copper sulphate, the proportion between the two reductions is about eleven or twelve. We see that the three values of the relation $\frac{D}{C}$ are to each other approximately as 1 : 2 : 3.

Thermic Value of the Three Functions of Orthophosphoric Acid and on its Constitution.—M. de Forcrand.—This memoir does not admit of useful abstraction, and is not of sufficient importance for insertion in full.

The Preparation and Properties of Fibroïne.—Leo Vignon.—Raw silk consists of two portions separable by means of different reagents. Industrially this is effected by means of boiling soap-lye, the result being 25 parts of the so-called gum and 75 parts of true silk. Mülser removed the gum by the action of boiling acetic acid, and obtained from 53 to 54 parts of fibroïne or true silk, and from 46 to 47 parts of soluble matter including the gum. Staedler treated raw silk for eighteen hours in the cold with a 5 per cent lye of soda. He obtained from 42 to 50 per cent of a substance which he considered as pure fibroïne. Cramer used water under pressure at 133° and obtained fibroïne equal to 66 per cent of the silk. Francezau acts upon raw silk with two boiling soap-baths and two successive baths of acetic acid at 8°. He obtains as a mean 75 per cent of fibroïne. The author treats with two successive baths of neutral white soap (150 grms. soap to 1500 c.c. of distilled water), respectively, for thirty to twenty minutes. After the first bath the skeins are rinsed in distilled water, first hot and then luke-warm. After the second soaping the silk is rinsed with boiling distilled water, with luke-warm distilled water, with cold distilled water containing per litre 10 c.c. of pure hydrochloric acid at 22°. Lastly, it was rinsed once with distilled water, and twice with alcohol at 90°. The yield is 75 per cent of a very white, brilliant, supple, tenacious and elastic material, which the author regards as fibroïne. Its specific gravity is 1.34. Its centesimal composition is—Carbon 48.3; hydrogen 6.5; nitrogen 19.2; oxygen 26. It contains only 0.01 per cent of mineral matter. If dissolved in concentrated hydrochloric acid it acts upon polarised light and is strongly lævo-rotatory.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. July, 1892.

This issue gives an account of the general Session held on May 27th for the distribution of prizes and medals. The Grand Prize of 12,000 francs, founded by the Marquis d'Argenteuil for the discovery of the greatest utility to French industry, was awarded to M. Berthelot, who is represented as the originator of organic synthesis.

August, 1892.

Report made by M. Troost, on Behalf of the Committee of the Chemical Arts, on the Automatic Manufacture of Vinegar, by E. Barbe.—This invention, which cannot be described without the accompaniment of the two large figures, dispenses with manual labour, the vats being fed mechanically with the utmost regularity by day and night.

MEETINGS FOR THE WEEK.

WEDNESDAY, 16th.—Society of Arts, 8. Opening Address of the 139th Session by Sir Richard E. Webster, Q.C.

THURSDAY, 17th.—Chemical, 8. "Fluosulphonic Acid," by Prof. Thorpe, F.R.S., and William Kirman, A.R.C.S. "The Interaction of Iodine and Potassium Chlorate," by Prof. Thorpe and George H. Perry, A.R.C.S. "Magnetic Rotation of Sulphuric and Nitric Acids and their Solutions, also of Solutions of Sodium Sulphate and Lithium Nitrate," by W. H. Perkin, F.R.S. "Note on the Refractive Indices and Magnetic Rotation of Sulphuric Acid Solutions," and "Hydrates of Alkylamines," by S. U. Pickering, F.R.S. "The Atomic Weight of Boron," by Prof. Ramsay, F.R.S., and Miss Emily Aston. Other papers.

ERRATUM.—P. 223, col. 1, line 10 from bottom, for "MS₂" read— $\frac{S}{M^2}$.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1721.

THE CONFIGURATION OF GRAPE-SUGAR AND ITS ISOMERS.*

By W. E. STONE, Purdue University.

THE researches of Emil Fischer upon the constitution and synthesis of sugars are well known through his numerous papers in the *Berichte*. The same have been reviewed in the *American Chemical Journal* (xi., 277, and xii., 357), and also in *Agricultural Science* (vi., No. 4). These researches have now proceeded so far, and the results harmonise so entirely with the theory of the asymmetric carbon atom, that Fischer proposes in two late papers (*Ber. Deut. Chem. Gesell.*, xxiv., 1836 and 2683), to assign certain specific configurations to those of the sugars which have been well studied.

Bold as this undertaking seems, his conclusions, all based on experimental data, conform to the requirements of the theory and are ingeniously and skilfully drawn.

According to the theory there may exist sixteen isomers of the structure of grape-sugar, and for those derivatives of the same which have symmetrical molecules, i.e., dibasic acids and hexavalent alcohols, ten different structures are possible. These structures are expressed by the following table taken from van't Hoff-Herrmann's paper, "Die Lagerung der Atome im Raume," in which the signs + or - are used to indicate the relative arrangement of the hydrogen and hydroxyl upon the four non-terminal carbon atoms of the sugar molecule, accordingly as their sequence conforms to the direction in which the hands of a watch move, or the reverse.

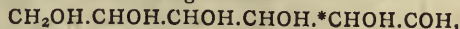
	11	12	13	14	15	16
	+	+	+	+	+	-
	+	+	+	+	-	+
	+	-	-	+	-	-
	-	+	-	-	-	-

	1	2	3	4	5	6	7	8	9	10
	+	+	-	-	-	+	-	-	-	-
	+	-	+	-	-	-	-	+	-	+
	-	+	-	-	+	+	+	-	-	+
	+	+	-	-	+	+	+	+	+	-

Of these it is evident that the arrangements 5-10 are identical with 11-16, so far as the alcohols or dibasic acids are concerned.

In order now to assign one of these configurations to grape-sugar upon the ground of experimental data it is necessary to consider the saccharic acid of which both optical forms are known. The d. saccharic acid is derived from both the d. and l. glucose (*Ber.*, xxiv., 521), they being stereoisomeric. Hence the two acids must be included in cases 5-10, since only such can be derived from stereoisomeric sugars. But of these numbers, 7 and 8 are optically inactive and therefore not to be considered. Of the remaining cases numbers 6 and 10 may also be rejected on the ground of the following experimental proofs.

Glucose and mannose differ from each other only in the configuration of the carbon atom, designated by an asterisk in the following formula—



and the same, of course, holds true for their derivatives (sorbite and mannite, gluconic and mannonic acids, and saccharic and manno-saccharic acids). The proofs of this hypothesis are strong as presented by Fischer:—

1. Mannose and glucose yield the same "osazon" (*Ber.*, xxii., 374).

2. Arabinose, by the addition of hydrocyanic acid, HCN, yields in the same reaction l. mannonic and l. gluconic acids (*Ber.*, xxiii., 2611).

3. Fructose is reduced by sodium amalgam to a mixture of mannite and sorbite (*Ber.*, xxiii., 3684).

4. Mannonic and gluconic acids, on being heated with pyridine or quinoline, are each transformed into the other (*Ber.*, xxiii., 800).

5. All attempts to separate mannonic or gluconic acids into different components have failed (*Ber.*, xxiii., 800).

Accepting these proofs of the relative structure of the above bodies, numbers 6 and 10 become impossible, for the following reasons. If saccharic acid, or what is the same thing, sorbite, had the structure 6—



or 10—



then the manno-saccharic acid or the mannite would have the structures 7—

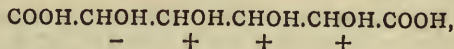


or 8—

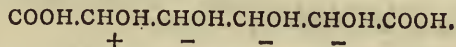


but these are both inactive combinations, while the mannite and manno-saccharic acid are both active.

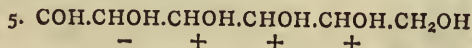
There remain, therefore, for the d. and l. saccharic acids only the two configurations 5 and 9, and since it is immaterial just which arrangement of hydrogen and hydroxyl one understands by + and which by -, Fischer assigns arbitrarily the configuration 5 to d. saccharic acid—



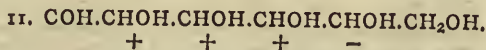
and 9 to the l. saccharic acid—



But corresponding to the d. saccharic acid are two aldehyd sugars, d. glucose, or grape-sugar, and the d. gulose, a synthetic product. These, being stereoisomeric, would have the configurations—

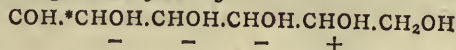


and

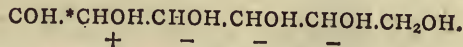


In order to assign one of these definitely to grape-sugar and the other to d. gulose, it is necessary to again extend our observations to another series of sugars, viz., the pentoses.

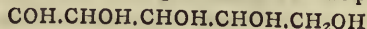
From one of these, arabinose, is derived l. glucose, and from the other (*Ber.*, xxiv., 529), xylose, comes l. gulose. For these latter (l. glucose and l. gulose) there remain the configurations 9 and 15—



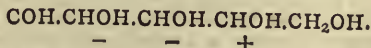
and



In these formulæ the asymmetric carbon atoms designated by the asterisk have been created by synthesis and do not exist in arabinose and xylose. Rejecting them, we have as the possible configurations of the two pentoses—



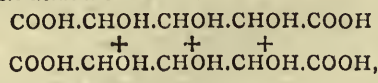
and



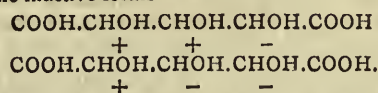
For the pentoses of the structure of arabinose and xylose (aldehyds) there are eight possible isomers, or for

* From the *American Chemical Journal*, xiv., No. 5.

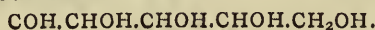
the corresponding dibasic acids or alcohols the number is four, of which two are active and two inactive systems. The theoretical configurations of the two active forms of the dibasic acids are as follows:—



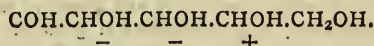
and of the inactive forms—



The optical behaviour of the acids or alcohols derived from arabinose and xylose would therefore serve to indicate in which of the above couples their configuration belongs. Here again the experimental testimony is clear, for both the arabite (upon the addition of borax) and the trioxo-glutaric acid from arabinose showed *lævo*-rotation. Arabinose, therefore, belongs to one of the two active systems, preferably the second, and its configuration would be as follows:—



The xylose, on the other hand, belongs to the inactive systems, since the xylite, even with borax, and the trioxo-glutaric acid from xylose, are both without influence upon polarised light. To the xylose therefore is assigned this configuration—



The configurations thus experimentally indicated for these sugars would of course hold for their derivatives among the hexoses, viz., the *l.* glucose and *l.* gulose, and from these the configurations of other members of the group are easily deduced, as follows:—

Hexose Sugars.

Aldoses.	COH	CHOH	CHOH	CHOH	CHOH	CH ₂ OH
<i>d.</i> glucose,	—	+	+	+	+	
<i>l.</i> glucose,	+	—	—	—	—	
<i>d.</i> gulose,	+	+	+	—	—	
<i>l.</i> gulose,	—	—	—	+	+	
<i>d.</i> mannose,	+	+	+	—	—	
<i>l.</i> mannose,	—	—	—	+	+	

(For galactose the experimental data do not yet justify a choice between the four possible configurations indicated by a study of the mucic and alloxanic acids.)

Ketoses. COH.CO.CHOH.CHOH.CHOH.CH₂OH

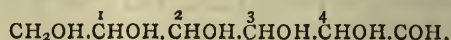
<i>d.</i> fructose,	+	+	+
<i>l.</i> fructose,	—	—	—

The mono- and dibasic acids and hexavalent alcohols derived from these sugars retain their respective configurations, and we have therefore reasonable experimental proof of the configuration of upwards of twenty bodies which are either sugars or closely related to them.

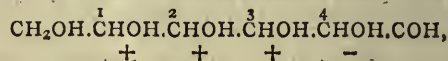
Fischer takes good care to remark, however, that these conclusions can only stand provided the theory of the asymmetric carbon atom is wholly in accord with the facts, and provided the oxidation of arabinose and xylose to the respective trioxo-glutaric acids occurs without intramolecular changes.

In the expressions used above, however, the signs + and — may easily be misinterpreted, and to prevent confusion, Fischer in a second paper presents these configurations in a clearer manner. Taking the familiar models of the carbon atoms, and constructing the sugar molecules according to the configurations proposed above, he develops graphic formulæ which have a new significance and permit an easy comparison of the different sugar molecules,

The four asymmetric carbon atoms may be designated by numbers, as follows—

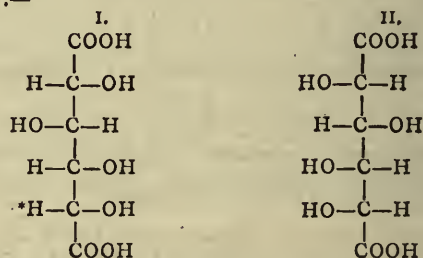


In the discussion of van't Hoff, upon which Fischer's deductions are based, the carbon atom 1 is compared only with 4, and 2 with 3. Consequently, in the configuration assigned to *d.* glucose or grape-sugar,—

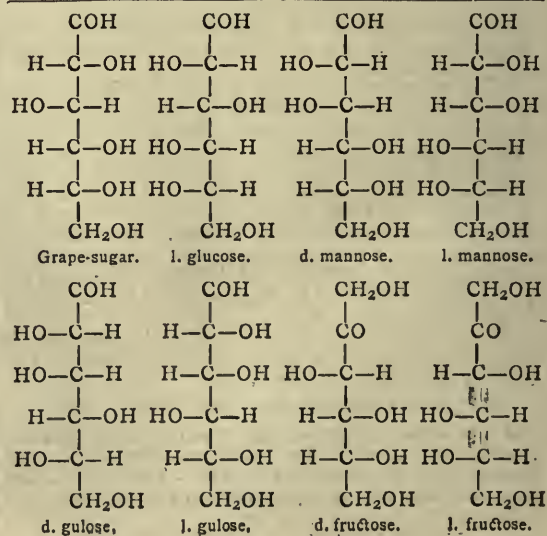


the arrangement of hydrogen and hydroxyl upon 1 is the opposite of that upon 4, while 2 and 3 are alike. If 1 be compared with 3 it is found that the arrangement is also the same. From a superficial examination the same would seem to follow for 1 and 2, but this is not the case, for the sign of 2 changes accordingly as it is compared with 3 or 1, as is apparent from the study of the model.

That is, the above expression for the configuration of grape-sugar permits of two interpretations, and to avoid confusion the structure is represented graphically as follows. By means of the flexible rubber models the molecules of the *d.* and *l.* saccharic acids are constructed; these are then placed upon a plane surface in such way that the carbon atoms lie in a straight line, when the hydrogens and hydroxyls arrange themselves on either side, and by projection present the following arrangements:—



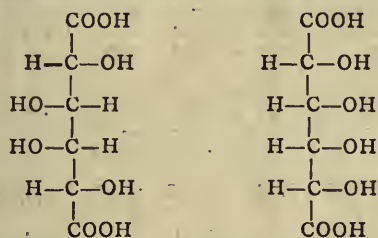
The same appearance is also obtained by the use of the inflexible wire models, arranging the carbon atoms in a vertical plane and regarding the structure from above. Fischer selects the first from the two above expressions for the *d.* saccharic acid, whereby it is again immaterial if, at starting, the arrangement of hydrogen and hydroxyl upon the starred carbon atom does or does



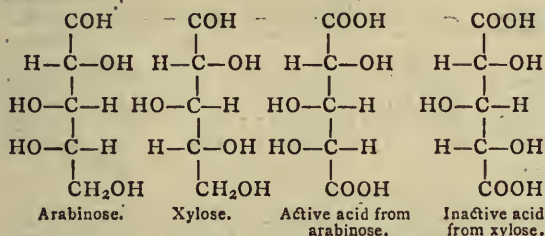
not follow the motion of the hands of a watch. From this, therefore, are derived the accompanying graphic representations of the configurations of the d. glucose and its isomers, the same being projections of models constructed on the basis of the configurations already indicated by the + or - signs. (See preceding column).

Of course these projection formulæ have a quite different significance from others of similar appearance which have been proposed before.

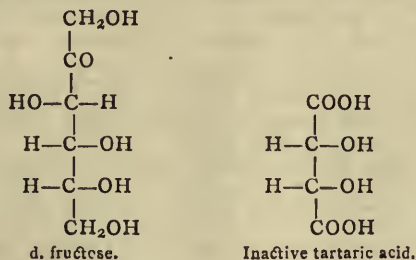
The projections for the two inactive dibasic acids of the dulcit series, which probably exist as the mucic and allomucic acids, are also given, as possibly furnishing some insight into the configuration of the galactose;



In the same way the following projections for the pentoses and their corresponding trioxo-glutaric acids are obtained:—



Working from these formulæ, the models of the molecules are easily constructed in which the + or - arrangement of each asymmetric carbon atom is readily seen. Their value is also apparent in the study of such reactions as increase or decrease the number of asymmetric carbon atoms, as an example of which the oxidation of fruit-sugar or levulose to inactive tartaric acid is given. The comparison of the projection formulæ of the two bodies renders it apparent how this reaction is possible.



Undoubtedly this insight thus obtained into the constitution and configuration of the sugars will point out the way to new reactions and to new explanations of known reactions; and in any event, Fischer's work, of which these last papers present the climax, constitutes the most notable contribution yet made to the subject.

Experiments on Bread and Biscuit.—M. Balland.—The author holds that the degree of hydration of bread depends much on the shape of the loaves. For equal weights a long loaf is preferable to one of a round form. —*Comptes Rendus*, cxv., No. 18.

SUCROSE, DEXTROSE, LEVULOSE:

THEIR QUANTITATIVE DETERMINATION WHEN OCCURRING TOGETHER.*

By F. G. WIECHMANN, Ph.D.

(Concluded from p. 239).

Experimental Test of Method.

Instruments Employed.—The polariscope used was a half shade instrument of Scheibler's make; every degree of its scale had been tested with a control tube of Schmidt and Hänsch.

The polarisations were all made with a Schmidt and Hänsch water-jacketed tube 200 m.m. long. The temperature of the solutions was determined by a small Centigrade thermometer graduated in tenths of a degree, made by the above firm, and of Jena normal glass. All readings in the polariscope were made by two observers; the observations were generally made every half degree Centigrade, from 17° to 20° C., but of course only the values obtained at 20° C. were placed on record.

Materials Used in Experiments.—The sucrose, the dextrose, and the levulose used in the experiments were all prepared under the writer's direction.

The sucrose was made from the purest granulated sugar (polarisation 99.9—100.0) by repeated washing with absolute ethyl alcohol. A determination of the specific rotatory power of the sucrose in a 10 per cent solution (10.0 grms. dry substance in 100 c.c.) gave $[\alpha]_D^{20} = +66.5$. The dextrose was prepared from commercial anhydrous dextrose by treatment with best blood carbon and by repeated crystallisation from absolute ethyl alcohol.

A determination of the specific rotatory power of the dextrose in a 10 per cent solution (10.0 grms. dry substance in 100 c.c.) gave $[\alpha]_D^{20} = +53.5$.

A determination of the reducing power of this material made by the method of J. Allihn, showed that 0.250 grm. dry substance of the dextrose reduced of metallic copper—

Determination 1 = 0.4655 grm.
Determination 2 = 0.4663 „

In Allihn's table 0.2499 grm. of dextrose corresponds to 0.4630 grm. Cu.

The levulose was prepared essentially according to the method of H. Ost (*Zeitschrift für Analytische Chemie*, 1890, p. 648) from inuline, prepared by H. Trommsdorff, of Erfurt. 100.0 grms. of inuline, 250.0 grms. of water, and 1.226 grms. of hydrochloric acid (specific gravity 1.20) were used. About three months after the work was commenced, and after being twice crystallised from absolute ethyl alcohol, the levulose obtained was tested.

Duplicate determinations of the specific rotatory power of this specimen were made with all possible care, and it was found that in a 10 per cent solution (10.0 grms. dry substance in 100 c.c.) the value of $[\alpha]_D^{20} = -81.9$.

A determination of the reducing power of this material on copper solution was made by Allihn's method for dextrose, exactly as quoted by Hönig and Jesser (*Zeitschrift des Vereines für Rübenzucker-Industrie*, 1888, vol. xxxviii., p. 1035), and this showed that 0.250 grm. of dry substance reduced of metallic copper—

Determination No. 1 = 0.4319 grm.
Determination No. 2 = 0.4309 „

Referring to Hönig and Jesser's investigation it will be seen that they found 0.250 grm. of pure levulose reduced 0.428 Cu.

The $[\alpha]_D^{20}$ value of this sample of levulose — 81.9 is identical with that quoted by Tollens (*Kurzes Handbuch der Kohlenhydrate*, p. 86) as obtained by calculation from data furnished by Dubrunfaut, Lescœur, and Morelle.

As the values for $[\alpha]_D^{20}$ found by Tollens and others differ greatly from this figure — 81.9 as well as from each other, there seems urgent need of an investigation to

* From the School of Mines Quarterly, xiii., No. 3.

Experiment.	1.*			2.*			3.*		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	-0.0033	0.0000	+0.0033	-1.370	-1.3728	-0.0142	-0.7100	-0.7036	-0.0064
Dextrose	3.00	3.02	+0.02	2.00	2.01	+0.01	2.50	2.51	+0.01
Levulose	2.00	1.98	-0.02	3.00	2.99	-0.01	2.50	2.49	-0.01

Experiment.	1.			2.*			3.*			4.		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	6.2465	6.2909	+0.0444	6.1788	6.1744	-0.0044	6.3142	6.2909	-0.0233	6.1918	6.2576	+0.0658
Sucrose	9.50	—	—	9.50	—	—	9.50	—	—	9.60	—	—
Dextrose	0.25	0.283	+0.033	0.20	0.197	-0.003	0.30	0.283	-0.017	0.10	0.149	+0.049
Levulose	0.25	0.217	-0.033	0.30	0.303	+0.003	0.20	0.217	+0.017	0.30	0.251	-0.049

Experiment.	1.			2.*			3.*			4.*		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	5.4395	5.3922	-0.0473	5.2364	5.2424	+0.0060	5.6426	5.6418	-0.0008	5.0463	5.0427	-0.0036
Sucrose	8.50	—	—	8.50	—	—	8.50	—	—	8.60	—	—
Dextrose	0.75	0.715	-0.035	0.60	0.605	+0.005	0.90	0.900	0.000	0.35	0.347	-0.003
Levulose	0.75	0.785	+0.035	0.90	0.895	-0.005	0.60	0.600	0.000	1.05	1.053	+0.003

Experiment.	1.			2.*			3.*			4.		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	4.6325	4.5934	-0.0391	4.2940	4.2938	-0.0002	4.9710	4.9928	+0.0218	3.9008	3.8611	-0.0387
Sucrose	7.50	—	—	7.50	—	—	7.50	—	—	7.60	—	—
Dextrose	1.25	1.221	-0.029	1.00	1.000	0.000	1.50	1.517	+0.017	0.60	0.571	-0.029
Levulose	1.25	1.279	+0.029	1.50	1.500	0.000	1.00	0.983	-0.017	1.80	1.829	+0.029

Experiment.	1.*			2.*			3.*			4.		
	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.	Required.	Deter.	Difference.
Polarisation in circular degrees	3.8255	3.7945	-0.0305	3.3516	3.3285	-0.0231	4.2994	4.3271	+0.0277	2.7553	2.7127	-0.0426
Sucrose	6.50	—	—	6.50	—	—	6.50	—	—	6.60	—	—
Dextrose	1.75	1.728	-0.022	1.40	1.383	-0.017	2.10	2.121	+0.021	0.85	0.819	-0.031
Levulose	1.75	1.772	+0.022	2.10	2.117	+0.017	1.40	1.379	-0.021	2.55	2.581	+0.031

determine whether the specific rotatory power of levulose varies according to the source from which it is prepared, according to the method of its preparation, or possibly according to both.

In these experiments, of course, the value of l in the formula for calculating the results of the analyses has been placed equal to -0.819 .

Record of Experiments.—In all, five series of tests were made. In the first series, dextrose and levulose only were used in order to study the behaviour of these two sugars in the absence of sucrose and when mixed in different proportions. In the remaining four series, sucrose, dextrose, and levulose were employed in varying proportions.

All polarisations were made on 10 per cent solutions (10.000 grms. dry substance in 100 c.c.) at the temperature of 20°C . All polarisations were made, as before stated, in a sugar polariscope, and transformed into circular degrees by multiplying with 0.346 .

The reliability of the gravimetric methods of determining the sucrose and the total reducing sugars having been amply demonstrated by a great number of experiments made at an earlier date, it was not deemed necessary to execute them in this work, and therefore the amounts of sucrose and of the total reducing sugars used in making the solutions are assumed as having been determined by analysis.

To correctly appreciate the meaning of the results here recorded, it must be remembered that 1° on the scale of

the sugar polariscope in these observations is equal to 0.346 circular degree. One-tenth of a degree on the sugar scale therefore corresponds to 0.0346 of a circular degree.

It will be granted that it is impossible to make an observation on a sugar scale which shall approximate closer to the truth than ± 0.1 of a degree. As this is equal to 0.0346 circular degree it will be but fair to regard all those observations made on the polariscope which come within these limits, viz., ± 0.0346 of a circular degree, as theoretically correct.

Making this allowance, inspection of the nineteen observations recorded in Series I. to V. inclusive show that of this number only six do not agree with the theoretical values. These exceptions are here given, and they exceed the limit of ± 0.0346 of a circular degree but slightly.

Series.	No.	Amount of difference.
II.	1	0.0098
II.	4	0.0312
III.	1	0.0127
IV.	1	0.0045
IV.	4	0.0041
V.	4	0.0080

Five of these determinations are but very little outside of the limits assumed, and even the poorest of them all, Series II., No. 4, would come well within the limits if ± 0.2 of a degree of the sugar polariscope be adopted as

the range of variation in the readings. With a more finely graduated instrument much closer readings could of course be made.

The Tables as given, however, show the amounts of levulose and of dextrose calculated from the polarisations actually obtained and without making any allowance whatsoever.

All experiments marked with a star would have yielded the results theoretically required, that is to say, absolutely correct values, provided that ± 0.1 of a degree on the sugar polariscope had been allowed for variation in the readings; and if a range of ± 0.2 of a degree on the sugar polariscope had been allowed in taking the readings, all experiments without exception would have shown the analysis to have determined the amounts theoretically required.

For exact scientific investigations, for instance, for accurately determining the kind and amounts of these three sugars in sugar-producing plants at different stages of their growth, &c., a delicate and finely graduated polariscope is required, but the work here recorded bears ample evidence of the fact that this method can be employed to advantage with the facilities provided for in every well equipped sugar laboratory.

THE REICHERT PROCESS FOR BUTTER, &c.

By H. DROOP RICHMOND.

In the CHEMICAL NEWS, vol. lxxvi, p. 199, Mr. J. A. Wilson contributes a paper under the above title; he states that exact agreement between two operators will not be possible, unless the same quantities of the same acid and alkali are used by each.

Mr. Wilson evidently argues from analogy between acetic and butyric acids, his experiments (*Journ. Soc. Chem. Ind.*, ix., No. 1, misprinted x. in original) having shown that the rate of distillation of acetic acid is affected by the presence of various salts in the solution distilled. He also states that this point has occupied notice; I cannot help thinking that "occupied" is a misprint for "escaped."

I may point out that Mansfeld, who uses caustic potash for saponification, states that his results are the same as those obtained by Wollny's (misprinted Woolny in Mr. Wilson's paper) method, and other experimenters have shown that the two agree within the limits of experimental error. In the *Stazioni Sperimentali Agrarie Italiane*, xxliii., No. 1, I have shown that butyric acid distils according to the following formula:—

$$y = 2.22x - 0.0151x^2 + 0.000031x^3.$$

x = quantity of distillate from 100 parts, and y = percentage of butyric acid distilled.

From this I calculate that when distilling 50 c.c. out of 75 c.c., 89.1 per cent should pass over, and when distilling 110 c.c. out of 140 c.c., 96.3 per cent should pass over. Actual experiment gave me 89.6 per cent and 96.9 per cent respectively when the quantities of acid and alkali used in the Reichert and Reichert-Wollny methods were added, and 89.7 per cent and 97.2 per cent when in addition 2.2 and 4.4 grms. of fatty acids were added.

I have also made a series of experiments, using Leffmann and Beam's modification, i.e., the use of glycerin for saponification in place of alcohol, and find a very slight increase in the quantity distilled, amounting on an average to 0.7 per cent.

I think that a reasonable variation of the amount of salts or other substances tending to raise the boiling-point will not affect the results within the limits of experimental error.

Mr. Wilson has pushed the case of analogy too far; in his paper before referred to, he quotes Duclaux's researches, but in the last one he has not borne them

sufficiently in mind. Duclaux shows that the volatility of the homologous fatty acids soluble in water increases with their molecular weight; thus, while under the conditions of the Wollny process, acetic acid furnishes less than 60 per cent in the distillate, butyric acid gives 96 per cent, and the higher acids more; there is not room for much variation when so high a percentage as 96 per cent is distilled. In Mr. Wilson's experiments on acetic acid, the distillation was pushed much further than in the Wollny process; allowing 2 c.c. for the vapour in flask and condenser, he had but 7 per cent left, while in the Wollny process there is 11½ per cent, and the concentration of the salts, and consequently boiling-point, is much less in the latter; it is in the highest degree probable that the excess found by Mr. Wilson, when salts were present, distilled over chiefly in the latter stages of the distillation.

Of course in an accurate scientific investigation the point raised by Mr. Wilson could not be neglected, but in an analytical method where the experimental error is 2 or 3 per cent, theory suggests and practice confirms that it is negligible.

50, Clanricarde Gardens, Bayswater, W.,
October 22, 1892.

REPORT ON POTASH.*

By Dr. GEORGE F. PAYNE, Atlanta, Ga.,
State Chemist of Georgia

THE work required by the Association of the reporter on potash for 1892 was an investigation as to whether the use of sodium chloride was essential in the Lindo-Gladding method of determining potash)

Four samples were prepared and were numbered one, two, three, and four.

Number one was a high grade sulphate of potash.

Number two was an acid phosphate with sulphate of potash in the form of kainit.

Number three was an acid phosphate with sulphate of potash in the form of kainit, and containing 5 per cent of double sulphate of alumina and ammonia.

Number four was identical with number three, with the substitution of 5 per cent of soluble sodium silicate in place of the double salt of alumina and ammonia.

The ingredients of each sample were first finely powdered and thoroughly mixed, then sifted through a very fine sieve, then again intimately mixed, and portions taken from forty different parts of the pile were well re-mixed and used for filling the bottles. Only the best xx superfine long taper corks were used, and were selected long enough to project well from the mouth of the vial to secure easy opening and air-tight re-corking. The corks were all well sealed with paraffin. With each package a circular was sent requesting that the determinations be made as soon as convenient after receiving samples to eliminate as far as possible any differences likely to occur from changes in the amount of moisture after bottling.

Each chemist was also requested to carry out the method as ordinarily managed in his laboratory, working each sample with and without sodium chloride, side by side, and as nearly as possible under exactly the same conditions.

Twenty-two chemists took part in the work, and their results are given in the Table.

Notes from Correspondents.

NORMAN ROBINSON, Florida.—As to the addition of NaCl, I have long since discarded it in regular laboratory work, as I never was able to satisfy myself that it was of enough benefit to pay for the additional expense in platonic chloride.

* For the Association of Official Agricultural Chemists of the United States.

Determination of Potash by the Lindo-Gladding Method with and without Sodium Chloride.

Names of Analysts and Location. Official Laboratories.	Sample No. 1.		Sample No. 2.		Sample No. 3.		Sample No. 4.	
	With NaCl.	Without NaCl.	With NaCl.	Without NaCl.	With NaCl.	Without NaCl.	With NaCl.	Without NaCl.
Norman Robinson, State Chemist, Tallahassee, Florida	48'83	48'70	1'58	1'59	1'47	1'46	1'40	1'41
F. S. Shiver, Assistant of State Chemist, Fort Hill, South Carolina (a) .. .	49'05	49'13	1'45	1'44	1'40	1'39	1'40	1'44
F. S. Shiver, Assistant of State Chemist, Fort Hill, South Carolina (b) .. .	49'00	—	1'45	—	1'40	—	1'32	—
P. L. Hutchinson, Assistant of State Chemist, Atlanta, Georgia .. .	49'05	49'15	1'50	1'48	1'51	1'40	1'48	1'40
J. F. Wilkinson, Assistant of State Chemist, Atlanta, Georgia .. .	49'13	49'12	1'50	1'52	1'47	1'42	1'36	1'34
F. B. Carpenter, Experiment Station, Raleigh, North Carolina .. .	48'94	—	1'61	—	1'48	—	1'56	—
Thos. L. Blalock, Experiment Station, Raleigh, North Carolina (a) .. .	48'76	48'76	1'63	1'63	1'48	1'46	1'48	1'47
Thos. L. Blalock, Experiment Station, Raleigh, North Carolina (b) .. .	48'96	49'10	—	—	—	—	—	—
Thos. L. Blalock, Experiment Station, Raleigh, North Carolina (c) .. .	48'90	48'91	1'59	1'58	1'51	1'48	1'46	1'45
Louis A. Voorhees, Experiment Station, New Brunswick, New Jersey .. .	49'23	49'19	1'49	1'46	1'35	1'36	1'36	1'37
Louis A. Voorhees, Experiment Station, New Brunswick, New Jersey .. .	49'27	49'29	1'51	1'52	1'38	1'42	1'36	1'37
Chas. S. Cathcart, Agricultural College, New Brunswick, New Jersey .. .	49'31	49'34	1'52	1'46	1'43	1'45	1'35	1'33
E. H. Farrington, Experiment Station, Champaign, Illinois .. .	49'29	49'00	1'77	1'64	1'77	1'66	1'62	1'51
Thos. L. Watson, Experiment Station, Blacksburg, Virginia, Assistant Chemist .. .	49'19	48'95	1'55	1'58	1'41	1'42	1'41	1'36
R. C. Kedzie, Agricultural College, P. O., Michigan .. .	48'75	48'69	1'55	1'53	1'54	1'51	1'67	1'65
Rudolf de Roode, Experiment Station, Morgantown, West Virginia .. .	48'96	48'96	1'52	1'55	1'42	1'42	1'37	1'39
Rudolf de Roode, Experiment Station, Morgantown, West Virginia .. .	49'04	49'04	1'57	1'53	1'48	1'46	1'39	1'37
C. B. Collingwood, Experiment Station, Tucson, Arizona .. .	48'62	48'38	1'51	1'47	—	—	—	—
Henry E. Curtis, Experiment Station, Lexington, Kentucky .. .	49'00	48'91	1'45	1'46	1'43	1'40	1'39	1'37
W. S. Sweetser, Experiment Station, State College, P. O., Pennsylvania .. .	49'26	49'28	1'69	1'57	1'58	1'53	1'45	1'43
W. S. Sweetser, Experiment Station, State College, P. O., Pennsylvania .. .	49'30	49'29	1'62	1'57	1'51	1'51	1'45	1'40
H. B. McDonnell, State Chemist, College Park, P. O., Maryland .. .	48'47	48'69	1'65	1'61	1'58	1'55	1'48	1'45
W. D. Bigelow, U.S. Department of Agriculture, Washington, D. C. .. .	48'56	48'31	1'49	1'58	1'57	1'37	1'47	1'42
Average .. .	48'994	48'961	1'554	1'538	1'484	1'456	1'439	1'417
Difference .. .	—	0'033	—	0'016	—	0'028	—	0'022
Unofficial Laboratories.								
Shepard Laboratory, Charleston, South Carolina .. .	49'88	49'80	1'87	1'91	1'75	1'74	1'66	1'55
Elwyn Waller, School of Mines, Columbia College, New York City .. .	49'67	49'17	1'60	1'46	1'61	1'53	1'59	1'59
Elwyn Waller, School of Mines, Columbia College, New York City .. .	49'89	48'71	1'62	1'52	1'56	1'52	—	1'53
Elwyn Waller, School of Mines, Columbia College, New York City .. .	—	48'21	—	—	—	—	—	—
Elwyn Waller, School of Mines, Columbia College, New York City .. .	—	48'69	—	—	—	—	—	—
H. T. Vulte, Assistant of Elwyn Waller, School of Mines, Columbia College, N.Y. .. .	48'88	48'54	1'66	1'58	1'58	1'53	1'58	1'52
B. C. Hinman, Assistant of Elwyn Waller, School of Mines, Columbia College, N.Y. .. .	—	48'99	—	1'51	1'67	1'40	1'41	1'40
F. S. Hyde, Student of School of Mines, Columbia College, New York City .. .	49'43	49'47	1'35	1'42	—	—	—	—
Average .. .	49'550	48'948	1'620	1'566	1'634	1'544	1'560	1'518
Difference .. .	—	0'602	—	0'054	—	0'090	—	0'042
Total average .. .	49'093	48'957	1'566	1'545	1'513	1'474	1'458	1'438
Difference .. .	—	0'136	—	0'021	—	0'039	—	0'020

F. S. SHIVER, South Carolina.—Determinations on line (a) were made by a modification of the Lindo-Gladding method as follows:—"After PtCl_4 has been added the solutions are evaporated to dryness on the water-bath, both of which are heated not quite to boiling. A little water is now added, about 1 c.c. in case of superphosphates, and about 2 c.c. in case of muriates, sulphates, and kainits. Five volumes of 95 per cent alcohol for each one of water are now introduced; the whole thoroughly mixed and allowed to stand one hour. Filtration and washing with 80 per cent alcohol and the NH_4Cl solution follow in the usual way." Results on line (b) were obtained by strictly following the official method.

THOS. L. BLALOCK, North Carolina.—Results on line (a) and (b) were obtained by evaporating until crystallisation took place on cooling. Those on line (c) were evaporated to dryness and moistened with water.

W. S. SWEETSER, Pennsylvania.—I find that when NaCl is used more washing is required in order to get uniform results.

H. B. McDONALD, Maryland.—The use of NaCl is certainly unnecessary.

ELWYN WALLER, New York.—Some of the results may differ from others on the same sample because of differences in percentage of moisture in the sample at different times, but the conclusion I should make is that without NaCl there was a tendency to irregularity, and, on the whole, lower results. The directions for the Lindo-Gladding method in the Bulletin do not seem to give the idea as to the amount of ammonium oxalate required. It says, "a little." I find that 10 grms. needed over 50 c.c. of (1 to 24) solution for complete separation of CaO . I analysed potassium by the same methods (theoretically = 9.90 per cent); result with NaCl = 9.816; result without NaCl = 9.836, which seems to be essentially the same.

H. J. WHEELER, Kingston, R. I.—I am very glad you are to take up the point in question, for past results indicate the possible benefits from such a course.

W. J. WILLIAMS, Wilmington, Del.—I may state that on several occasions I have tested this question and have found that if the potash after treatment with half-strength sulphuric acid is thoroughly ignited to whiteness, so that no free sulphuric acid is left, the addition of NaCl makes no more difference in results than will be found in ordinary analytical differences. I believe it is unnecessary.

The mass of evidence here presented furnishes strong and convincing proof that the use of NaCl is unnecessary in potash determinations.

Dr. Gladding in 1885 presented his results to his association upon chemically pure sulphate of potash. Three determinations without NaCl gave him 100.95, 102.81, and 101.45 per cents respectively of sulphate of potash. Three determinations of the same salt made with the addition of NaCl gave 100.01, 100.16, and 99.95 of sulphate potash, obviating the inaccuracy he supposed to exist from the presence of free sulphuric acid when the NaCl was not used.

Two hundred and nine results obtained by twenty-two chemists show no advantage in the use of NaCl. Instead of obtaining something which was not potash and hence higher figures without NaCl, the general tendency has been to lower results when NaCl was omitted. This difference was quite small, but is present in a large majority of the determinations, and is naturally to be expected, if the NaCl is not needed, on account of the difficulty of washing out the sodium salt. About two-thirds of the analysts who took part in the work obtained slightly higher figures with NaCl than without it, the reverse of Dr. Gladding's experiences. In about three-fourths of the determinations the differences between with and without NaCl, by the same chemist, were less than one-tenth of one per cent, and in about half of the results the differences were less than one-twentieth of one per cent.

Recommendations.

The following recommendations are made:—

(1) In superphosphates, page 187, second line, in place

of the words "a little oxalate of ammonia" insert "a sufficient quantity of oxalate of ammonia to throw down all lime present."

On lines numbers nine and ten strike out the words "5 c.c. of a solution of pure NaCl (containing 20 grms. NaCl to the litre), or its equivalent of dry salt."

On line number eleven change the word "are" to the word "is."

(3) Sulphate of potash, kainit, &c., page 187, second and third lines, in place of the words "a little oxalate of ammonia," insert "a sufficient quantity of oxalate of ammonia to throw down all lime present."

On page 188, second line from top, strike out the words "add 0.25 gm. of NaCl," and insert the word "add" between "and" and "15 c.c."

On page 188, fifth line from top, strike out the words "0.25 grms. NaCl and."

Page 188, fifth line. Put the word "all" in place of the word "these," and in the sixth and seventh lines, after the words "to remove all the double chloride of platinum and sodium," add the words "if present."

It is also recommended that the reporter on potash for the coming year put himself in communication with the Association of Experiment Stations in Germany, and any other accessible official chemists in other countries, and secure, as far as possible, their co-operation in our comparative work of the coming year.

Bearing on this subject the following quotations are translated from a letter of the German Kali syndicate of July 29th, 1892:—

"As yet, the Association of Experiment Stations of the German Empire has not accepted any definite methods for potash determination. Not many stations use the Stassfurt methods. A variety of methods are in use according to the preference given by different chemists. We have made a request of the Association of Agricultural Experiment Stations of the German Empire to take steps for securing uniformity in this question. Privy Councillor Maerker, who is President of the Committee on Fertilisers, has already declared that he will make a motion at the next convention in September to test the Stassfurt methods and eventually to recommend their introduction."

Further on will be found the methods of potash determination used at the Anhalt mines at Stassfurt, Germany, as communicated by their chief chemist, Dr. Zimmerman, with his criticisms of other methods. His work, while most excellent with the Stassfurt method, shows want of experience with the Lindo-Gladding method, as in these analyses the difference between the highest and lowest is over one per cent, a difference for which the method is certainly not to blame, when so many American official chemists are constantly working it with results equally as close as he obtains with the Stassfurt method.

We wish accurate methods and quick ones, and are always ready to grasp anything good. The Stassfurt method is submitted to the Association with the suggestion that it be taken up and studied through our next reporter on potash. If it is equally as good as the Lindo-Gladding, and much quicker, as claimed, it will be very valuable.

The London CHEMICAL NEWS (vol. lxx., pp. 22, 32) contains an interesting article by Drs. Gooch and Hart upon the spectroscopic detection and estimation of potassium.

There is a point in the determination of potash which is not given the proper weight and attention by manufacturers, and it is that of mixing. Unmanipulated potash salts give analytical chemists far less trouble, as a rule, than mixed fertilisers.

To mix fifty pounds of rough muriate of potash with a ton of fertiliser, as is sometimes done, and secure a perfect mixture, is almost impossible. Weights and measures are handled roughly and quickly, and some manufacturers appear to believe that badly mixed goods,

after standing and becoming disintegrated by the sulphuric acid, actually become well mixed. If a solution is made up from a fertiliser, and several determinations made from that same solution, they tally beautifully; but make separate weighings from your supposed well-mixed sample, and results never check so well. Manufacturers think a "wet mix" ought to be perfect, but as all the ingredients are weighed independently for each ton, and in the South negroes usually do this work, and bricks, in some establishments, are used as weights, it is easy to see how each ton must vary, and the only wonder is that the goods run as uniformly as they do. To illustrate this, fourteen analyses are here given of goods made by the same formula and claimed to be identical, which were drawn out of separate batches from a large and well-equipped factory. These samples show imperfect mixing, whether from too rough weighings or bad manipulation it is difficult to decide, with only small samples drawn by other parties. Attention is also called to the varying amounts of moisture, insoluble phosphoric acid, and ammonia. Moisture varies 8.30 per cent, insoluble phosphoric acid 4.13 per cent, ammonia 0.77 per cent, and potash 0.95 per cent.

Moisture.	Insol. P_2O_5 .	Avail. P_2O_5 .	Ammonia.	Potash.
14.95	2.33	9.95	2.37	2.16
15.00	2.24	10.30	2.29	2.19
13.50	4.22	9.34	2.26	2.03
16.85	1.60	10.17	2.33	2.24
16.55	2.49	9.41	2.29	2.12
16.60	2.43	9.21	2.25	2.20
16.55	2.62	9.41	2.12	1.70
16.25	2.36	9.79	2.00	1.80
17.75	1.00	10.90	1.93	1.60
18.85	0.41	9.82	2.33	2.33
19.45	0.26	10.11	2.53	2.30
21.80	0.09	9.76	2.44	2.55
19.05	0.90	9.46	2.50	2.35
18.10	0.64	10.11	2.70	2.45

(To be continued).

NEW METHODS FOR QUANTITATIVE ANALYSIS.*

By A. BAUMANN.
(Concluded from p. 237).

THE separation of sulphur has an injurious effect, in as far as it occludes starch iodide, and thus produces an excessive consumption of solution of thiosulphate.

In presence of merely very small quantities of sulphides, the expulsion of hydrogen sulphide may be omitted without injury. The sulphur which is separated on the decomposition of the polysulphides does not interfere on account of its finely pulverulent form.

Whilst the determination of the mineral acids succeeds without difficulty, the separation of the iodine by the organic acids is only effected by degrees. The transformation in solutions of tartaric and oxalic acid is not complete until twenty-four hours have elapsed. For acetic acid a still longer time is required. The determination of organic acids by the iodometric method appears, therefore, injudicious, but Gröger regards it as probable that the method may be applicable if the organic acids are caused to act upon the iodine salts with the aid of heat.

Baumann utilises the reaction which ensues between free acid and a mixture of potassium iodate and iodide for the determination of free mineral acids in the gas-volumetric way, proceeding as follows:—

He puts into the larger space of the development vessel of the azotometer a knife-point full (from 1 to 2 grms.) of

very finely powdered potassium iodate, dissolves it in a little water, adds about 10 grms. potassium iodide, and then runs in an accurately measured quantity of the acid, which must be greatly diluted. Iodine is separated and remains dissolved in the excess of potassium iodide. The liquid is diluted to about 40 c.c. if its volume is smaller. The attached glass cylinder is charged with hydrogen peroxide and potassa lye in the manner previously described, the stopper is closed, and after the temperature has become equalised the iodine is determined gas-volumetrically. The number of the c.c. of gas found is multiplied with the number in the author's hydrogen table, and thus the weight of the hydrogen of the acid is obtained.

In order to find the weight of the acid the product is multiplied by the equivalent concerned.

No very strong acids can be directly determined by the gas-volumetric method, but only acids of about the strength of those which are titrated with decinormal alkali.

Of acids at 3 to 6 per cent we take 2 c.c. for analysis if the measuring tube of the azotometer holds only 50 c.c. A double quantity may be used if a burette holding 100 c.c. is available. Stronger acids are made up with water to a given volume, and an aliquot part is used for determination. A larger quantity of weaker acids may be used, e.g., 30 to 60 c.c. of decinormal acid.

According to Baumann, the determination of the organic acids may be effected if certain conditions are observed. Tartaric, oxalic, and acetic acids liberate an equivalent quantity of iodine if they are heated to 70° for thirty minutes with the mixture of potassium iodide and iodate.

NOTES ON SOME ANCIENT DYES.*

By EDWARD SCHUNCK, Ph.D. F.R.S.

THE fragments of ancient dyed fabrics which I have examined I owe to the kindness of Mr. R. D. Darbishire. They are specimens from a lot found by Mr. Flinders Petrie, in a tomb at Garob, Lower Egypt, supposed to date from 400—500 A.D. They were used apparently for filling the mummy cases where required, not strictly speaking as grave clothes. My object in examining them was to ascertain, if possible, what were the materials employed in producing the various colours seen on them. The fabrics examined consisted almost entirely of wool. Here and there in the warp of some of the specimens were threads, conspicuous for difference in colour, consisting of linen. The following colours could be distinguished:—Blue, yellow, green, red, maroon, purple or claret, black. I will take them in the order named.

Blue.—The colour of the fabric was a dull medium blue. On treatment with hot caustic lye a great part of the wool dissolved. The residue, which was dark blue, having been filtered off, washed, and dried, was treated with boiling aniline, to which it communicated a bright blue colour. The blue solution having been filtered boiling, deposited on cooling a quantity of blue crystalline scales, which, after being filtered off, washed with alcohol, and dried, were found to consist of indigo-blue. On being heated in a tube they gave a sublimate of regular crystals, blue by transmitted, copper coloured by reflected, light; they dissolved in concentrated sulphuric, giving a blue solution, and the solution in aniline showed the absorption-spectrum of indigo-blue. It is evident, therefore, that indigo in some form or other was the material used in dyeing this colour.

Yellow.—The colour of the patches dyed yellow was so evidently faded, and showed so little intensity, as to make it very uncertain whether analysis would lead to any precise result; the examination was therefore omitted.

Green.—Of the material dyed this colour, I had but a

* Zeit. für Angew. Chemie und Zeit. für Analytische Chemie.

* From *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, vol. v. Series 4.

small quantity, but it was sufficient to allow of some conclusion regarding the means whereby the colour was produced. On being treated for some days with dilute hydrochloric acid it imparted to the latter a deep yellow colour. The portion left by the acid, after being washed and dried, yielded indigo-blue on treatment with boiling aniline. It is probable, therefore, that the colour was produced by first dyeing the fabric with indigo, then treating with some mordant, such as alum, and, lastly, dyeing with some yellow colouring matter, most likely of vegetable origin. With the small quantity of material at my disposal, I found it impossible to ascertain the nature of the yellow colouring matter employed.

Red.—This was the most pronounced, and at the same time the most interesting, of the colours examined. The colour of the fabric was a full deep red. It might be called a Turkey red: the dye, in fact, proved on examination to be a kind of Turkey red as having the characteristic properties of that dye.

On being burnt, the fabric left a considerable quantity of ash, consisting of calcium sulphate, alumina, aluminium phosphate, ferric oxide, and silica. A large portion of this ash no doubt represents the mordant employed in producing the colour. On treatment with hot dilute hydrochloric acid the fabric lost its red colour and became yellow. After removal of the acid by washing with water, and pressing between blotting paper, treatment with boiling alcohol deprived the wool of the greater part of the yellow colour, a faint tinge only being left. The deep yellow alcoholic liquid obtained left on evaporation a reddish-brown amorphous residue. This, on being treated with a boiling solution of alum, dissolved in part, yielding a pink fluorescent liquid, which had exactly the same colour, and showed precisely the same absorption bands as a solution of purpurin from madder in alum liquor. On adding hydrochloric acid to the pink solution and heating, the colouring-matter was precipitated in orange-coloured flocks, the liquid becoming almost colourless. The flocks after being filtered off and washed with water dissolved easily in boiling alcohol, yielding a yellow solution, which, on spontaneous evaporation, left a quantity of dark yellow needles arranged in rosettes. These needles dissolved in caustic alkali, giving a cherry-red solution, which showed the absorption bands of purpurin. The solution, on exposure to air and light, became colourless.

Some of the precipitated colouring-matter, on being employed in the usual way for dyeing a bit of calico to which various mordants had been applied, yielded colours exactly like those obtained with purpurin from madder, *i.e.*, the alumina mordant gave a bright red, the iron mordant dull purple to black tints. The matter left undissolved, after repeated treatment with boiling alum liquor, was still highly coloured. It dissolved easily in alcohol, the solution leaving on evaporation a brown amorphous residue, which remained soft even after long standing. This residue consisted for the most part of fatty matter, but it also contained some colouring-matter insoluble in alum liquor. That this colouring-matter was alizarin seemed probable, since the colour which the mixture imparted to alkaline lye resembled that of an alkaline solution of impure alizarin.

These experiments lead to the conclusion that the red colour of the fabric was produced by dyeing with some kind of madder, either wild or cultivated, the fabric having been previously treated with a mixed aluminous and ferric mordant, and then probably oiled,—that it was, in fact, really a kind of Turkey red.

Maroon.—The dull chestnut colour of this fabric presented a striking contrast to the bright red of the preceding. Its constitution was, however, similar. Having treated it in the same way as the other, I found that the colouring-matter must have been derived from madder; fatty matter was also present, but the mordant contained a larger proportion of ferric oxide,—a fact which sufficiently explains the brown tint of the dyed fabric.

Purple.—The fabric in which this colour was seen was made up of a pale yellow warp, and a weft of a dull purple or claret colour. The latter colour was found to be due to an intimate mixture of red and blue, for the threads, on examination under the microscope, were seen to consist partly of red, partly of blue fibres, the former predominating. The two sets of fibres had, of course, been mixed before spinning. The blue fibres were certainly died with indigo, the red probably with madder.

Black.—The colour of the black fabric, like that of the green, was a compound of two colours, one overlying the other. Under the microscope the individual threads appeared grey. On treatment with a mixture of alcohol and hydrochloric acid they changed colour, a yellow liquid being obtained, while the fabric itself now appeared blue, and after washing and drying yielded indigo by appropriate treatment. The yellow alcoholic liquid was found to contain purpurin. The colour may be supposed to have been produced in the following manner:—The woollen fabric having first been dyed blue was mordanted, to use a modern phrase, and then dyed with madder, the two colours together producing the effect of black.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

THE facility with which many metallic formates could be reduced to the metallic state by heat, or in the case of silver and mercury, even by the action of light, having led to the hope that they might be employed with particular advantage in electrolysis, the following series of experiments were made upon solutions of copper, zinc, and cadmium formates, in order to ascertain the effect of dilution, temperature, and pole separation, as well as the conditions necessary in order to effect their quantitative estimation and separation. The current was generated by a battery of ten cells, of the "crowfoot" type, each cell being 3.1 d.m. in height, by 1.9 d.m. in diameter, and having a capacity of two litres; the dimensions of the zincs were 1.5 c.m. by 1.5 c.m., and of the radiating copper plates constituting the positive pole 1.5 c.m. by 1.5 c.m. By means of this battery a comparatively uniform current of 2.8 c.c. electrolytic gas per minute was generated after the cells had been in use for some time.

The strength of the current was measured by means of an ordinary voltmeter, and was ascertained before and after the completion of the experiment. For the deposition of small quantities of metal, thick platinum-foil electrodes were used, 3.8 c.m. wide, and immersed to the depth of 3.8 c.m. in the solution. For quantities above 0.05 gm. they were unsatisfactory, the metal showing a great tendency to separate in a spongy condition at the edge. In the earlier determinations a platinum dish was used, weighing about 67 grms., and having a capacity of 150 c.c.; in the later ones a dish weighing 117 grms., and with a capacity of 275 c.c., was employed. The results obtained with the larger dish were necessarily somewhat less exact than with the one of smaller size. The positive pole consisted of a thick platinum wire, the lower portion of which was wound into a horizontal spiral. In some of the separations it was found expedient to substitute for the spiral a small platinum crucible 2.5 c.m. in height and 2.8 c.m. in diameter, closed by a cork, through which passed a copper wire in contact with the bottom of the crucible. In order to regulate the distance between the poles, a filter stand was used, having inserted on its movable arm an ordinary binding screw, to which the positive pole was attached.

The following formates were prepared:—

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxix., No. 136.

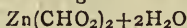
Copper Formate.

This salt was made by precipitating cupric oxide from a hot solution of copper sulphate, by means of caustic potash; the precipitate was washed by decantation until free from traces of potash; it was then dissolved in formic acid having the sp. gr. 1.015, obtained in the usual way from oxalic acid and glycerin, through which a current of steam was allowed to pass in order to prevent too great a rise of temperature, with the consequent production of decomposition products; the salt was allowed to crystallise out by spontaneous evaporation in a current of warm air, and re-crystallised. An abundant crop of large blue monoclinic crystals was obtained, having the composition $\text{Cu}(\text{CHO}_2)_2 \cdot 4\text{H}_2\text{O}$, effervescing in dry air, soluble in eight parts of water, and changed by boiling to the sparingly soluble basic salt $\text{Cu}(\text{CHO}_2)_2 \cdot 2\text{Cu}(\text{HO})_2$.

Zinc Formate.

A solution of ordinary crystallised zinc sulphate was treated with an excess of sodium carbonate, heated almost to boiling, freed by decantation from soluble impurity, and dissolved in hot formic acid. The solution was evaporated down and allowed to stand, after filtering off a slight precipitate that formed on boiling, and which gave the iron reaction with potassium sulphocyanate.

Monoclinic prisms having the formula—



separated out, isomorphous with the cadmium salt, permanent in the air, and soluble in twenty-four parts of water at ordinary temperature.

Cadmium Formate.

This salt was prepared by dissolving cadmium obtained by distillation *in vacuo*, in nitric acid, neutralising with a hot solution of potassium carbonate, washing by decantation until free from soluble carbonate, and dissolving in formic acid. Large monoclinic crystals separated out, having the composition $\text{Cd}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$, permanent in the air, readily soluble in water.

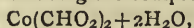
(NOTE.—The formulæ of copper and cadmium formates are given as follows:— $\text{Cu}(\text{CHO}_2)_2$ and $\text{Cd}(\text{CHO}_2)_2$ in the last edition of Watts' "Dictionary of Chemistry," differing from all other authorities. Experiments made to settle the question resulted in the formulæ assigned, which is in accordance with the ones usually given).

Lead Formate.

Solutions of lead acetate and sodium formate were mixed and allowed to stand. Large white anhydrous rhombic crystals gradually separated out in radiating needles, sparingly soluble in cold water, more readily in hot, but with partial decomposition into free acid, and a basic salt of variable composition.

Cobaltous Formate.

A hot solution of cobaltous sulphate was neutralised with caustic soda solution, washed by decantation until free from all but traces of the precipitant, dissolved in formic acid, filtered, and allowed to evaporate in a current of warm air. The salt separated in crusts, consisting of indistinct crystals having the composition—



dissolving with difficulty to a reddish coloured solution.

Manganous Formate.

This salt was prepared from manganous carbonate precipitated from a hot solution of manganous sulphate, by means of sodium carbonate added to alkaline reaction and decanted as rapidly as possible until free from all except very slight traces of soluble salts. It was then dissolved in formic acid and allowed to crystallise very slowly. The crystals thus obtained were allowed to re-crystallise. The crystals are small pale reddish monoclinic prisms, soluble in fifteen parts of water, and contain two molecules of water of crystallisation.

Nickel Formate.

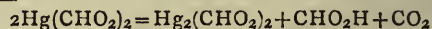
A solution of nickel chloride was treated with a slight excess of sodic hydrate, washed several times by decantation with hot water, dissolved in acid, and evaporated down. A greenish crust formed, made up of very small bright green needles— $\text{Ni}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$.

Ferric Formate.

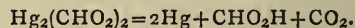
Ferric chloride was treated with excess of a solution of ammonia, washed with hot water, and allowed to digest in formic acid at a temperature which was not allowed to exceed 70° , until the hydrate of iron had completely dissolved, which required several hours. The deep red solution was allowed to crystallise by spontaneous evaporation. Yellowish red needles crystallising in radiating tufts separated out, which formed a light loose coherent powder. When dried at a moderate temperature, it was readily soluble in cold water with an acid reaction. Aqueous solutions on warming became turbid from the partial decomposition of the salt into ferric hydrate and free acid. A similar decomposition takes place in solutions at ordinary temperatures after standing for some time. (The foregoing salt was made in preference to ferrous formate on account of its greater solubility).

Mercuric Formate.

Mercuric oxide was dissolved in formic acid, but on warming the solution slightly it decomposed into the very sparingly soluble white mercurous formate, carbon dioxide, and formic acid, according to the following equation:—



and—



The precipitate was grey in colour from the presence of free mercury. The tendency to decompose is such that in solution at ordinary temperatures these changes take place readily in the light and, with more slowness, even in the dark. The "ous" salt comes out in minute shining crystals, very insoluble in water, and on continuous warming becomes entirely converted into free mercury. The formates of silver, bismuth, and tin are not prepared, as they were not considered available for various reasons.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, November 7, 1892.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Miss Emily Drummond, J. J. Duveen, Esq., Edward Johnson, Esq., George Blundell Longstaff, M.D., F.R.C.P., Robert Dobie Wilson, Esq.

The Special Thanks of the Members were returned to Mr. Thomas G. Hodgkins, of Brambletye Farm, Setauket, Long Island, New York, for his most valuable gift of \$100,000 (£20,523 6s. 11d.).

The Special Thanks of the Members were returned to the Goldsmith's Company for their generous grant of £1000 "for the continuation and development of the valuable original research which the Society is engaged in carrying on; and especially for the prosecution of investigations on the properties of matter at temperatures approaching that of the zero of absolute temperature."

The Special Thanks of the Members were returned for the following Donation: Mr. F. D. Mocatta, £50, for carrying on Investigations on Liquid Oxygen.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Theine versus Tannin; or, China Tea versus Indian and Ceylon Tea. By STUART CRANSTON (Glasgow). London: W. B. Whittingham and Co.

THE title of this remarkable pamphlet might lead any cursory reader to suppose that Indian and Ceylon tea contained no theine! Yet the author admits (p. 6) that Indian tea contains more theine than that from China. According to the analyses quoted, the Chinese teas are also much poorer in tannin; but this is not an original difference: it depends merely on the process of manufacture. The pamphlet before us admits that the excess of tannin might be eliminated with advantage. There are also some other difference not here emphasized. Chinese tea is worked up by hand, whilst the Indian leaf is scarcely touched except by machinery. Now, anyone who knows the hands of John Chinaman would greatly prefer any articles which he had *not* touched.

The use of tea along with albumenoid foods—as in the so-called “tea-dinner”—is a great mistake. Whatsoever truth there is in Mr. Cranston’s pamphlet might, we submit, have been put in a more patriotic manner.

CORRESPONDENCE.

NEW SILVER ORE.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, vol. lxvi., p. 42, is a “Note on the Recent Discovery of a New Silver Ore,” by Mr. H. N. Warren, in which he asserts that the well-known argentiferous kaolin of Broken Hill, N.S. Wales, was first noticed this year by some travelling mineralogists. As a matter of fact, large quantities of specially rich kaolin were first noticed in April, 1885, by Mr. W. Jamieson, one of the original developers of the Broken Hill on the south half of Block 12. Fifty tons were sent to Melbourne while the B. H. Proprietary Company was being floated in July, 1885, and yielded 750 ounces of silver to the ton.

Shortly after its discovery the ore was known to contain chloride, bromide, and iodide of silver.—I am, &c.,

W. PERCY WILKINSON,
Assistant to the Government Analyst.

Melbourne, Victoria, October 4, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 18, October 31, 1892.

Observations on M. Berthelot’s Communication presented at the Last Session of the Academy of Sciences.—M. Schloesing.

Reply to the Foregoing Paper by M. Berthelot.—A controversy on priority in the announcement of the condensation of nitrogen upon soils by the agency of microphytes.

The Dissociation of Barium Peroxide.—H. Le Chatelier.—The dissociation of barium peroxide is a phenomenon less simple than it is supposed. It requires

the intervention of watery vapour and the action of presence of a melted mixture of barium hydroxide and barium peroxide. Hence the conditions of the tension of dissociation are not rigidly fixed.

A Limited Reaction.—Albert Colson.—In studying the action of sulphuretted hydrogen upon metallic salts dissolved in benzene free from water, the decomposition is not complete, and it gives rise to a peculiar state of equilibrium. A very small quantity of water alters the results and ensures total decomposition.

The Fixation of Free Nitrogen by Plants.—Th. Schloesing and Em. Laurent.—In the conditions of the author’s experiment, oats, colza, and potatoes did not fix free nitrogen in a measurable quantity.

Purification of Sewage by Ferric Sulphate.—A. and P. Buisine.—The authors conclude that it is possible to treat large volumes of sewage continuously by means of ferric sulphate, and to obtain valuable products from the mud.

Ptomaines Extracted from Urine in Erysipelas and Puerperal Fever.—Dr. A. B. Griffiths.—The former ptomaine is a white substance forming orthorhombic lamellae, soluble in water, with a slightly alkaline reaction. Its formula is $C_{11}H_{13}NO_3$. The ptomaine found in puerperal fever has the same properties, but its composition is $C_{22}H_{19}NO_2$. Both these ptomaines are intensely poisonous.

Hermerythrine: A Respiratory Pigment found in the Blood of Certain Worms.—Dr. A. B. Griffiths.—There are in the blood of invertebrate animals at least four respiratory pigments containing iron in their molecule.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. vii. and viii., Nos. 15 and 16.

On Acetone-Resorcine.—H. Causse.—The compound of acetone and resorcine is in small prismatic crystals, anhydrous, and fusible at 212° to 213° . It is insoluble in water, benzene, chloroform, and dry ether, but soluble in alkaline hydrates and carbonates. Its composition, dried at 30° , is $C_{15}H_{16}O_4$. The reaction is general. Besides resorcine, pyrogallol and pyrocatechine combine very readily with acetone, but hydroquinone forms no combination.

Light Oils obtained in the Distillation of Bog-Head.—A. Brochet.—Among the numerous ethylenic carbides which may be formed during pyrogenation, those of the linear chain exist almost alone. There are only small quantities of isobutylene and traces of trimethylene. Hexylene is the highest term of the series which is formed in this medium. Then follows benzene, toluene, dipropylene, and finally coal-tars, which on distillation give products of an offensive odour.

Preparation of Zinc, Manganese, and Cadmium Sulphites.—G. Denigés.—The composition of these salts is: zinc sulphite, $(SO_3Zn)_2 + 5H_2O$; manganese, $SO_3Mn + 2H_2O$; and cadmium, $(SO_3Cd)_2 + 3H_2O$.

On Quinine Iodomethylates.—E. Grimaux.—This memoir does not admit of useful abstraction.

Syntheses in the Ethylenic Hydrocarbides under the Influence of Zinc Chloride.—Jean Kondakoff.—This extensive memoir also is not adapted for abstraction.

In Reference to a Note by M. Hantzsch on Carbacetylacetic Ether.—P. Genviesse.—A controversial note.

Facts to Contribute to the History of Gum Arabic.—A. Béchamp.—The author, in common with Dubrunfaut, holds that the molecule of gum consists of dextrorotatory and levorotatory members. If this hypothesis is admitted, the explanation of the fact that the

nitro-gums are dextrorotatory follows from the theory of M. Guye. In these compounds the nitric acid is connected by substitution with the dextrorotatory term or terms, and determines the dextrorotation of the molecule which was originally levorotatory.

Researches on Nickel and Cobalt.—M. Lachaud and Ch. Lepierre.—In a former communication they described the action of ammonium bisulphate ammonium on the salts of iron (*Comptes Rendus*, April 11th, 1892). They now describe the substances obtained with nickel and cobalt.

Action of Ammonium Sulphate upon Glass.—M. Lachaud and Ch. Lepierre.—The action of ammonium sulphate seems to be specific, and this action is the more curious as it disaggregates the glass at a relatively low temperature.

Condensation of Chlorobenzile with Phenol and with Mono- and Dimethylaniline.—M. St. Kempinski.—The substance obtained is insoluble in water, in acids, and in ligroine, but very soluble in water, alcohol, benzene, &c., and in caustic alkalis. It is a red powder, which does not appear to possess tinctorial properties.

Action of Phosphorus upon Copper.—M. Granger.—The compound obtained by the author corresponds to the formula Cu_3P_2 . If ignited in an inert gas they lose phosphorus and leave as a residue Abel's phosphide, Cu_3P .

Mercury Phosphide.—M. Granger.—The compound obtained is Hg_3P_4 .

Change of Sign of the Rotatory Power.—J. A. Le Bel.—This paper does not admit of useful abstraction.

Tri- and Tetra-sulphonic Indigotine Acids.—P. Juillard.—All the author's analyses establish the presence of tri- and tetra-sulphonic indigotine acids in the state of mixture. The colouring matter obtained is doubtless identical with Bailliey's purple-blue.

Direct Transformation of Aniline into Nitrobenzene.—M. Prudhomme.—The group NH_2 of aniline is directly converted into NO_2 . This transformation is very interesting since we know only one procedure for passing from aniline to nitrobenzene, that of Sandmeyer.

Certain Ethers of Gallic Ether and of Dibromogallic Acid.—Alex. Biatrix.—An account of ethyl dibromogallate and methylgallate.

Gummy Matters and the Peptic Matters. A New Organised Ferment of Cherry Gum.—F. Garros.—If cherry gum is left with water in a flask very full and stoppered with wadding, in one and a half months the cherry gum is entirely dissolved, and there is a deposit at the bottom of the flask consisting of members smaller than those of beer-yeast. It is this ferment which has effected the solution of the cherry gum.

MISCELLANEOUS.

The Late Professor Stas.—According to the *Chem. Zeitung*, the Belgium Academy of Sciences unanimously petitioned the Government to purchase the valuable apparatus and chemicals of the departed *savant* as of high historical scientific value, and deposit them in a public museum so as to obviate the danger of their being dispersed. The Academy petitioned also for the necessary funds for a new edition of all the memoirs of Stas which are no longer to be procured in the book-trade. After a long delay the Academy received a complete refusal. It was alleged that "the schools were sufficiently supplied with apparatus and preparations." This reply gives a decisive measure of the level which Belgian statesmen have reached as regards Science. We thus see that the English Government does not stand isolated in being unfavourable to Science and her followers.

Society of Arts.—The following courses of Cantor Lectures will be delivered during the coming session of the Society of Arts:—Prof. Vivian Lewes, "The Generation of Light from Coal-Gas, and its Measurement," on Nov. 21, 23, Dec. 5, 12; Dr. J. A. Fleming, "The Practical Measurement of Alternating Electric Currents," on Jan. 30, Feb. 6, 13, 20; Prof. W. Chandler Roberts-Austen, C.B., F.R.S., "Alloys," March 6, 13, 20; Mr. Lewis Foreman Day, "Some Masters of Ornament," April 10, 17, 24, May 1; Mr. C. Harrison Townsend, F.R.I.B.A., "The History and Practice of Mosaics," May 8, 15.

MEETINGS FOR THE WEEK.

MONDAY, 21st.—Society of Arts, 8. "The Generation of Light from Coal-gas," by Prof. Vivian B. Lewes.
— Medical, 8.30.
TUESDAY, 22nd.—Royal Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8.
— Photographic, 8.
WEDNESDAY, 23rd.—Society of Arts, 8. "Cremation as an Incentive to Crime," by F. Seymour Haden, F.R.C.S.
— Geological, 8.
THURSDAY, 24th.—Royal, 4.30.
— Institute of Electrical Engineers, 8.
FRIDAY, 25th.—Physical, 5. "Experiments in Electrical Magnetic Fields, Constant and Varying," by E. C. Rimington and E. Wythe Smith.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1722.

THE VOLUMETRIC DETERMINATION OF THE ALKALOIDS.

By ALFRED H. ALLEN.

THE paper of M. Barthe, reproduced from *Comptes Rendus*, which appears in the CHEMICAL NEWS (vol. lxvi., p. 223) ought not to be absorbed into chemical literature without a protest. M. Barthe believes that his observations are novel, but such of them as are accurate have been established previously by several observers, and are now well known to chemists interested in the alkaloids.

The actual facts respecting the behaviour of the alkaloids with phenolphthalein are stated in the following passage from a paper read by me before the Chemists' Assistants' Association in January, 1891, and printed in the *Pharmaceutical Journal* ([3], xxii., 772) a few weeks later:—

"It is interesting to observe that phenolphthalein and Poirrier's blue, CLB, which may be used as indicators for very feeble acids, are absolutely indifferent to the majority of the alkaloids and organic bases. Even aniline and pyridine, which have such strongly marked basic characters, are perfectly neutral to phenolphthalein. The same is true of strychnine, quinine, aconitine, and, with the limitation already mentioned, morphine. Hence the salts of these bases, such as hydrochloride of aniline, sulphate of quinine, and nitrate of aconitine,* can be titrated with caustic alkali and phenolphthalein, just as if the respective acids were in an uncombined state. According to E. Léger, cicutine and codeine are exceptions to the general rule of indifference of the alkaloids to phenolphthalein; and, according to P. C. Plugge, nicotine and conine also exhibit an alkaline reaction. A curious exception to the general behaviour of alkaloids is also presented by atropine and its isomers (as also hematropine), which in the free state strongly redden phenolphthalein. This property, however, does not exist in alcoholic solution—a fact which marks a curious distinction between these alkaloids and the mineral alkalies, the alcoholic solutions of which react perfectly with phenolphthalein."

I do not claim any originality for the above statements, which simply express the results of various observers supplemented by my own experience; but the following applications of this principle are novel. In the analysis of a mixture of cinchona alkaloids, the cinchonidine is usually precipitated from a neutral solution by potassium tartrate, and the precipitate washed with cold water (thereby causing an uncertain loss), dried, and weighed. If, instead, the precipitate be washed once with a saturated solution of the precipitant (which has very little solvent action), and the filter containing the precipitate of cinchonidine tartrate and the adherent Rochelle salt be immersed in boiling water, the alkaloid can be determined in a few minutes by adding a drop of phenolphthalein solution and titrating with N/20 caustic alkali. As Rochelle salt is perfectly neutral to phenolphthalein, and as alkaloidal tartrates act just like an equivalent amount of free tartaric acid, the weight of alkaloid can be readily calculated from the measure of standard alkali used. An exactly similar method is applicable to the treatment of the precipitate of quinidine hydriodide.

In sharp contrast to the indifference of nearly all the alkaloids to phenolphthalein is their behaviour with methyl-

orange. To this indicator most of the alkaloidal salts are rigidly neutral, and hence all the alkaloids and organic bases of which the behaviour has hitherto been examined—except urea, caffeine, theobromine, and (perhaps) aniline—may be titrated with methyl-orange and a standard mineral acid, and with much greater facility than when litmus is used.

In titrating an alkaloid with methyl-orange it is rarely convenient to employ an aqueous solution of the base. A solution in proof spirit can be used, but the indicator is much less sensitive under such conditions. I have found it preferable, especially when the alkaloid is much coloured, as is frequently the case in assaying bases directly extracted from their sources, to dissolve the alkali in a little ether, chloroform, amyl alcohol, or other suitable immiscible solvent. The solution is placed in a small stoppered cylinder, together with a few c.m. of water coloured with a drop of methyl-orange solution. On then gradually dropping in the standard acid and agitating thoroughly after each addition, it is easy to observe the end of the reaction, as the interfering colouring-matter remains in the immiscible layer and presents a marked contrast to the red colour of the aqueous liquid. By using ether as a solvent, and titrating with N/50 hydrochloric acid, I have obtained very satisfactory determinations of aconitine and its allies, even when working on as little as 0.030 grm.

A similar plan can be adopted for the titration of the morphine crystals obtained in the assay of opium, amyl alcohol being used as the solvent; or the alkaloid can be simply dissolved in excess of standard acid, and the solution titrated back with alkali, using methyl-orange as the indicator of neutrality.

Sheffield, November 14, 1892.

NOTE ON THE ESTIMATION OF OLEIN.

By L. DE KONINGH, F.C.S.

THE *Analyst* (vol. xvii., p. 118) contains an article on the determination of olein by Mr. O. Hehner, and the author comes to the conclusion that the process founded upon the relative solubilities of the fatty lead salts in ether is utterly untrustworthy. This opinion will perhaps cause works chemists to distrust a process which I am not in the least inclined to give up; a process which I still consider to be, under certain conditions, one of the most elegant and accurate methods to be met with in organic commercial analysis.

It is far from my intention to criticise Mr. Hehner's iodine figures, as these are no doubt very accurate in their way; but my object in writing these lines is to point out how to apply the process when great accuracy is required. Nobody must expect to get a reliable result when the oleic acid is largely exceeded by the fixed fatty acids; in fact, it is not unlikely that in such a case the operator will find none at all. But the remedy is a simple one. A proper equilibrium must be restored, and this is best done by dissolving the fatty acids in boiling alcohol and searching for the oleic acid in the mother-liquor from which the bulk of the solid acids has crystallised out.

Analysts familiar with the process must have noticed that the clear ethereal solution of the lead oleate sometimes gets turbid and deposits a more or less abundant flocculent precipitate. This precipitate is, I have good reason to believe, a basic lead oleate, as the normal lead salt seems to behave in a slight degree like normal bismuth nitrate. If now the analyst notices that such has taken place, or if the extraction has not gone quite so readily as usual, the best way is to decompose the residual lead soap by means of hydrochloric acid, to re-crystallise the liberated acids from alcohol, and to once more apply the process to the mother-liquor. In fact, the well known principle of re-dissolving and re-precipitating should be applied.

* Ordinary nitrate of aconitine is not a neutral salt; it contains $B_2(HNO_3)_3$.

As regards the lead salts of palmitic and stearic acid, they are absolutely insoluble, as may be easily proved by adding ammonium sulphide to their supposed ethereal solution. Of course, I am not prepared to say what a few months' extraction in the Soxhlet may do, as I believe that even barium sulphate might disappear at last, but under normal conditions the ether process will be found a very suitable one for those fats which are mainly composed of stearin, palmitin, and olein.

In conclusion, I should like to ask Mr. Hehner to ascertain for himself the iodine absorptions of the oleic acids from tallow, lard, and also once more for cotton-seed oil, for which I have found the figures 90, 93, and 135 when using the process described in *The Analyst*, vol. xiv., 64-65.

ON CHROMIUM CAST STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

At the last meeting of the Iron and Steel Institute (October, 1892), Mr. R. A. Hadfield contributed a highly valuable paper on "Alloys of Iron and Chromium." We were especially interested with the handsome results obtained by Mr. Hadfield in the manufacture of chromium steel projectiles, as we took a prominent part in the manufacture of the same in Russia, at the Poutiloff Iron and Steel Works, St. Petersburg. We worked by the process adapted by the French works of J. Holtzer, Unieux, Loire.

Great care must be taken in casting ingots for projectiles; rising ingots are rejected. Such metal contains only small amounts of silicon and manganese. Good sound metal contains on the average 0.18 per cent of silicon and 0.20 per cent of manganese. The sum of phosphorus and sulphur is not to exceed 0.03 per cent (sulphur better not more than 0.015 per cent). Chromium steel has a pasty appearance, but if prepared in a Siemens gas crucible furnace, has enough heat in itself to remain fluid in the crucible for ten to fifteen minutes, after the withdrawal of the latter from the furnace.

Care must be taken in handling the ingots just only cast. Throwing them on wet ground, or placing them where the wind, rain, or snow can cool them, should be avoided, as cracks in the ingots may result. The best method is to bury the cast ingots in ashes. For the forging of ingots between stamps the metal should be heated not higher than 1000° C.; the same temperature is to be observed during the annealing of the forged projectiles before they are sent to the turning and boring lathes.

In 1890 we commenced the manufacture of 12 inch projectiles for the navy. The specimens from the annealed ingots gave the following results:—

Diameter of specimen, 16 m.m.
Length of specimen, 100 m.m.

Specimen. Nos.	Elastic limit. (In kilograms. per square m.m.)	Breaking strain.	Elongation. Per cent.
1.	49.5	93.1	7.2
2.	54.1	95.4	8.1
3.	41.5	88.1	7.3
4.	40.3	85.6	8.0
5.	45.3	95.5	6.5

From one of the reception lots, viz., 100 12-inch projectiles, three were selected by the Government inspectors and gave the following results.

Only two shells were fired at the polygon of Ochta, near St. Petersburg. The 16 inch compound armour plate was manufactured at the Kolpino Works by the Cammell method; the gun was made at the Obouchoff Steel Works. Both works belong to the Government, and are situated some few miles off St. Petersburg.

The two shells penetrated the plate and were found on the other side of the plate at a distance of—

First projectile 7000 feet.
Second projectile . . . 5250 feet.

They showed no cracks, and altered only very slightly in their dimensions.

We used ferrochrome coming from Boucau (France), containing only 0.08 per cent of phosphorus and 0.03 per cent of sulphur. It is a very pure alloy. The Russian ferrochrome prepared by the Demidoff Works cannot be used in the manufacture of projectiles. It contains a rather poor quantity of chromium and too much of phosphorus, as shown by our analyses made on different samples:—

Sample No.	Chromium.	Phosphorus.
1.	35.30 per cent.	0.411 per cent.
2.	38.81 "	0.409 "
3.	40.45 "	0.421 "
4.	40.50 "	0.558 "

On the other hand, the Boucau samples are very rich in chromium, containing not less than 49 per cent up to 60 per cent of the metal.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1892.

By WILLIAM CROOKES, F.R.S.,
and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, November 8th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Throughout the month of October the water supply to the Metropolis continued to be of excellent quality, and was found not to differ appreciably in character from that of the preceding month, or materially from the supply of the past six months inclusive, taken as a whole. Of the entire rainfall of the month, amounting at Oxford to a little over 3 inches, fully 2½ inches fell during the last five days of the month, with the result of bringing the river into flood, but not affecting the character of the then supply. The entire series of the 182 samples examined were found to be well-filtered, clear, and bright; and their degree of colour-tint to be low for the season of the year.

The following Table of the results furnished by the Thames-derived supply, taken for illustration, shows the smallness of the extent of the monthly variation at present noticeable in the amounts of organic matter present in the water,—the excess of organic carbon in the Octo-

ber supply above the mean for the six months' supply, or 0.01 part in 100,000 parts of the water, being quite infinitesimal.

Thames supply.	Ratio of brown to blue tint. Means.	Oxygen required for oxidation. Means.	Organic carbon per 100,000. Means.	Organic carbon per 100,000. Maxima.
Past 6 months	10.4 : 20	0.039	0.117	0.155
September ..	15.5 : 20	0.042	0.118	0.145
October ..	15.0 : 20	0.047	0.127	0.155

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

SEPARATION OF MALIC ACID FROM SUCCINIC, CITRIC, AND TARTARIC ACIDS.

By C. MICKO.

THE process depends on the behaviour of the acids with baryta water.

Free succinic, citric, or tartaric acid is not completely precipitated by baryta water either in cold or heat. But the precipitation succeeds under especial circumstances if the acids are present in the form of neutral or acid potassium salts.

In concentrated solutions of acid or neutral potassium succinate an excess of baryta water effects an incomplete precipitation in the cold. On boiling, or on prolonged heating, to a temperature near the boiling-point, succinic acid is completely eliminated, save in very trifling traces. After standing at rest for half an hour the precipitate takes a granular crystalline texture, but if allowed to stand for a week perceptible quantities pass again into solution.

The solutions of potassium citrate, acid or neutral, behave with baryta water in a similar manner. The precipitate, which appears in the cold, if slowly heated to gentle ebullition, is suddenly converted into a voluminous paste, which is a characteristic of citric acid.

Potassium tartrate, neutral or acid, behaves differently. A complete precipitation is not produced by an excess of baryta water either in heat or cold. After standing for twenty-four hours at the ordinary temperature, a large part of the tartaric acid is precipitated. If we then pass into the filtrate a slow current of carbonic acid until the reaction is neutral or faintly alkaline, and then add anew an excess of baryta water, after standing for twenty-four hours at the ordinary temperature a complete precipitation of the tartaric acid ensues. The experiment succeeds at a gentle warmth, but not in heat.

In mixtures of potassium succinate, citrate, and tartrate no complete precipitation of the acids is obtained. Even after introducing carbonic acid into the filtrate and a renewed addition of baryta water, traces of all the three acids could still be detected after standing for twenty-four hours. It seems as if the liberated potassa prevents complete precipitation. The attempt was consequently made to neutralise the potassa by an addition of barium acetate, and in this manner a complete precipitation of the several acids was effected.

A mixture of the acids, however, did not give a complete precipitation, even in presence of potassium acetate, if the carbonic acid was introduced in the cold. But it was found advantageous under such conditions to introduce carbonic acid in heat until the liquid became neutral or very faintly alkaline. But as no complete precipitation of the acids was effected even in this manner, the main quantity of the baryta was thrown down in heat by the introduction of an excess of carbonic acid, and the filtrate was evaporated down to a small residue. If this residual liquid was again treated in the manner above described, the filtrate obtained was free from tartaric, citric, and succinic acid.

In solutions of potassium malate, baryta water produces a faint turbidity only after prolonged boiling, and no precipitate occurs in presence of alkaline acetates.

On the basis of these experiments the author proposes the following method for separating malic acid from the succinic, citric, and tartaric acid:—

The solution which contains the acids as potassium salts, and which should have a faint acid reaction, is evaporated down in a flask until it amounts only to 10 to 15 c.c., mixed with 0.5 gm. barium acetate and an excess of baryta water, and gradually heated to ebullition. This is kept up for two minutes, with frequent agitation, and, after cooling, the flask is closed and allowed to stand for from twelve to twenty-four hours. The bulky precipitate is then filtered off and washed with baryta water. The washing must not be continued too long, as otherwise the precipitate begins to re-dissolve.

The filtrate is then heated to incipient ebullition, the heating is interrupted, and carbonic acid is then introduced until the reaction is neutral or slightly alkaline. An excess of baryta water is added, the mixture is again allowed to stand for twelve or twenty-four hours, and the precipitate is filtered off and washed with baryta water.

The filtrate is heated and treated with a current of carbonic acid to precipitate the excess of baryta, and the precipitate is filtered off and washed with hot water. The filtrate is then, after the addition of two to three drops of acetic acid (to prevent separation of baryta during concentration), evaporated down to 10 or 15 c.c., and again heated to remove the last traces of succinic, citric, and tartaric acids. Carbonic acid is passed into the warm liquid without filtration until the reaction is neutral or faintly alkaline, and after adding baryta water until the reaction is distinctly alkaline it is again allowed to stand for from twelve to twenty-four hours. It is then filtered, and the precipitate is washed with baryta water as above. The filtrate thus obtained contains all the malic acid, and is free from the three other acids.

The baryta is precipitated in heat with carbonic acid, the barium carbonate is washed with hot water, the filtrate is concentrated to a small volume (after the addition of two to three drops of acetic acid), and the remaining baryta is precipitated with a slight excess of potassium carbonate. The filtrate acidulated with acetic acid is evaporated down to a small residue, another drop of acetic acid is added, and, as soon as it is cold, 5 c.c. of a solution of lead acetate (1 : 5), previously acidulated with acetic acid, and 120 c.c. of alcohol at 80 per cent are poured in, stirring continually.

The precipitation is effected in a flask, which is stoppered and allowed to stand for forty-eight hours. The large excess of alcohol is necessary, and much potassium acetate is present in proportion to the potassium malate, and the former salt prevents complete precipitation if the addition of alcohol is insufficient.

The precipitate is filtered off and washed with alcohol at 80 per cent, at first cold and then hot. The filtrate, which is often turbid, is heated in a flask with a reflux cooler until the solution is clear. The flask is then stoppered and set aside for forty-eight hours. The small quantities of lead bi-malate separated out are washed with cold alcohol. The dried precipitates are united, dissolved in hot alcohol, and the lead is separated with sulphuric acid. The weight of malic acid is calculated from the lead sulphate obtained.

The results are very satisfactory. Though the values are too low (about 96.3 per cent in place of 100), precipitation is preferable to the calcium chloride method, since the latter is not available in presence of potassium acetate.

The author has tried direct precipitation with lead acetate in pure solutions of potassium malate. The results are rather too high (about 102 per cent), as small quantities of lead acetate are carried down.

If lead malate is precipitated in heat with alcohol we certainly obtain a fine granular precipitate, but the results

are much too high, since the precipitate partially melts and the inclosed lead acetate cannot be removed by washing.—*Zeitschrift für Analytische Chemie*.

ATTEMPT AT A GENERAL METHOD OF ORGANIC SYNTHESIS.

By RAOUL PICTET.

THE object of this research is to define in a precise manner a general method for obtaining synthetically any natural substance whatever. The way to be adopted to fix the programme of the successive necessary reactions follows from a primary hypothesis, which will serve as a postulate in these researches. In this preliminary paper space does not permit us to expound anything more than this hypothesis,—the foundation of all our study on chemical synthesis. We shall then give a series of experimental verifications of the fundamental hypothesis. Lastly, we shall describe the first applications of this theory to divers chemical syntheses of the aromatic series.

Fundamental Hypothesis.

We admit that all physical and chemical phenomena result from the conflict of two attractions: the attraction of *matter for matter* and the attraction of *matter for ether*. According to the distance of the atoms among themselves, the attraction of matter for matter receives the names of *gravitation, cohesion, affinity*. We do not know the value of the Newtonian function applied to *cohesion* or to *affinity*. We admit that the atoms are immersed in the ether but remain impenetrable to this fluid. In virtue of this fact they are subject to the laws of the principle of Archimedes, as they always displace their own volume of ether.

The attraction of matter for ether follows a special law different from the Newtonian law, extending to all distances. Our fundamental hypothesis may be thus expressed:—On reducing every chemical phenomenon to the action of two masses of matter falling upon each other along the right line passing through their centres of gravity, we admit that the two functions of the distances representing the two attractions enable us in every case, and without exception, to find three positions of equilibrium upon this right line—that is to say, three positions where the resultant of the two attractions is null. Further, the equilibrium is stable in the two extreme positions and instable in the mean position.

[The remainder of this memoir cannot be reproduced without constant reference to the diagram given in the original].—*Comptes Rendus*, cxv., p. 708.

THE DETERMINATION OF PHOSPHORIC ACID IN BASIC SLAGS.

By DR. ADOLF F. JOLLES.

THE views on the solvent in the determination of phosphoric acid in basic slags differ widely from each other. We may particularise two directions, one of which recommends the samples to be opened up with concentrated sulphuric acid and the other with hydrochloric acid.

At a meeting of Austrian managers and officials of agricultural experimental stations, held at Vienna on August 30, 1890, Dr. von Lorenz recommended the use of Maercker's process exactly as it had been proposed at Bonn Congress of the Experimental Stations in 1889. I have had repeated opportunity to analyse basic slags both by the molybdenum method and by Maercker's process, and I always obtained differences in the percentage of phosphoric acid which were proportional to the percentage of lime. These differences are to be referred to the well-

known fact that the gypsum liberated on opening up the slags with concentrated sulphuric acid incloses particles of calcium phosphate which are thus withdrawn from the solution. I have found similar losses of phosphoric acid when using hydrochloric acid.

Last year H. and E. Albert, of Biebrich, on the basis of numerous experiments, have recommended the following method for determining total phosphoric acid in basic slags, and have introduced it into the laboratory of their works:—

Five grms. of the finely-ground slag are moistened with a little water in a flask of the capacity of 500 c.c. and boiled upon the sand-bath with 40 c.c. of hydrochloric at 16°–20° Bé. The mixture is boiled until there remain only a few c.c. of a thick paste of silicic jelly, allowed to cool, and a little water is added. It is then shaken until the thick clots of silicic acid are very finely divided, made up to 500 c.c. with water, and filtered. 50 c.c. of the filtrate are mixed with 15 c.c. of Joulie's solution (i.e., 400 grms. citric acid made up to 1 litre with ammonia of specific gravity 0.9), and then precipitated in the ordinary manner with magnesia mixture, ignited, and weighed. There is no danger of obtaining silica in the magnesia precipitate, since many experiments have proved that the condensation of the hydrochloric solution to a thick jelly is sufficient to render the silica insoluble. If a standard solution of uranium is at hand we dissolve (if the presence of silica is suspected) the moist precipitate on the filter in a little nitric acid, and titrate in the usual manner.

I have had this process and, as a check, the molybdenum method carried out in numerous analyses of basic slags in my laboratory, with the result that the Albert method, both gravimetrically and volumetrically, yielded far too high results in comparison with the molybdenum method. The cause of these discrepancies can only be sought for in the imperfect elimination of the silica.

I cannot in my analyses confirm the above quoted statement of H. and E. Albert, since I have always been able to recognise the presence of silica in the precipitates of magnesia. I have, then, dissolved the magnesia precipitate in hydrochloric acid, evaporated it to dryness, heated the residue to 120° in the air-bath, re-dissolved in hydrochloric acid, and weighed the silica.

The differences varied according to the time of boiling, and I obtained results agreeing with those of the molybdenum method only on boiling the basic slag meal in hydrochloric acid, evaporating completely to dryness, and heating in the air-bath to 120°. This method may thus be modified by evaporating the silica to perfect dryness, retaining the further course of the analysis.

As for the volumetric determination, I have dissolved the moist precipitate of ammonium magnesium phosphate in a little nitric acid, neutralised it with ammonia, dissolved it in acetic acid, and titrated with solution of uranium. The results obtained have, by accident, coincided with the gravimetric results according to Albert, so that I at first believed that no silica was present in the precipitate of ammonium magnesium. In fact, however, I found in every precipitate ponderable quantities of silica; therefore, according to the check titration with uranium solution I should have obtained less phosphoric acid than by weighing, which was not the case. There occur here also sources of error which act in opposite directions and which may even mutually compensate each other.

The most important defect of this method lies in the untrustworthiness of the indicator. I have frequently observed that the brown colour does not appear at once, but not until the lapse of some minutes.

I believe that in the analysis of manures the motion accepted at the Congress of Chemists at Hanover in 1889 ought to be kept in mind, according to which "the volumetric determination of phosphoric acid is regarded as no longer adequate to the demands of the age and is declared untrustworthy."

For the volumetric determination of phosphoric acid in basic slag, I venture to propose the following modification of the method of H. and E. Albert:—

Five grms. of fine slag-meal is moistened with a little water in a capsule boiled with 40 c.c. of hydrochloric acid at about 20° Bé. and evaporated to perfect dryness. The residue is heated to 120° in the air-bath, moistened with hydrochloric acid when cold, taken up in water, and filtered. The filtrate is made up to 500 c.c., 50 c.c. of which are mixed with citrate solution, and the phosphoric acid is precipitated in the ordinary manner with magnesia mixture, when the precipitate is dried, ignited, and weighed.

With this procedure I have obtained results which agreed fairly with those of the molybdenum method. In cases where the analyst wishes to check himself or other chemists, and in disputed cases, the molybdenum method is exclusively admissible.—*Zeit. fur Anal. Chemie.*

REPORT ON POTASH.*

By Dr. GEORGE F. PAYNE, Atlanta, Ga.,
State Chemist of Georgia

(Concluded from p. 254).

A DESCRIPTION AND CRITIQUE OF VARIOUS METHODS OF POTASH ANALYSIS.

Methods of Potash Analysis as used in the Mines of Anhalt.

(1) DETERMINATION of potash alone in carnallite, kainit, and sylvinit: 100 gr. of the well mixed sample are put into a graduated flask, holding 1000 c.c., and dissolved by boiling with 500—600 c.c. water, acidulated with 10 c.c. hydrochloric acid. The purpose of adding hydrochloric acid is to bring polyhalite in solution, that might be present in the salts, and which is difficult to dissolve in pure water. After dissolving and cooling, the flask is filled up to the mark. The solution after thorough mixing is filtered through a dry filter. 100 c.c. of the filtrate, corresponding to 10 gr. substance, are put into a 500 c.c. flask by means of a pipette. After the addition of 200—300 c.c. water, the solution is heated to boiling and the sulphuric acid accurately precipitated with normal chloride of barium solution, containing 104 gr. of the dry salt in one litre. The volume of the precipitate is calculated from the amount of barium solution used, and from the specific gravity of the barium sulphate. After cooling, the flask is filled up with water so much above its mark as equals the volume of the calculated barium precipitate, and, after thorough mixing, the solution is filtered again through a dry filter. 50 c.c. of this filtrate, corresponding to 1 gr. substance, are evaporated upon the water-bath with a sufficient amount of platinum chloride. The residue of potassium-platinum chloride is washed with 90 per cent alcohol, dried at 120°, and weighed.

(2) If it is desired to determine separately the quantity of potash present in the form of sulphate, and in the form of chloride, as for example in kainit, and in sulphate of potash, or, if it is to be determined whether potassium sulphate is in combination with a proportionate amount of magnesium chloride, as in kainit, or in combination with magnesium sulphate alone, as in schoenit, it becomes necessary to determine besides potash the percentage of chlorine, sulphuric acid, lime, magnesia, the total alkalis, water, and the residue insoluble in water. For this purpose, 100 gr. of the sample are dissolved, the solution is filtered, the filter washed, and the filtrate made up to one litre; a part of the liquid is taken for the determination of sulphuric acid, by precipitating with barium chloride, and another part for the determination of lime and magnesia. For the determination of the alkali chlorides, 100 c.c. of the solution, corresponding to

10 gr. substance, are acidulated with hydrochloric acid, and after heating to boiling, the sulphuric acid is completely precipitated with barium chloride, with the precaution of using not more of the barium solution than is necessary for the complete precipitation. 50 c.c. of the filtered solution, corresponding to 1 gr. substance, are evaporated to dryness in order to drive off the hydrochloric acid. Chloride of magnesium is decomposed by igniting with oxalic acid, or with oxide of mercury. After ignition, the residue is moistened with a little carbonate of ammonia for the purpose of rendering the calcium oxide that may have been formed into calcium carbonate.

The alkali chlorides, which are now entirely free from lime and magnesia, are weighed, and potassium chloride is determined by means of platinum chloride. The amount of chloride of sodium results by deducting chloride of potassium from the mixed chlorides. For the water determination, 5 gr. of the sample are ignited, and the loss of weight is determined. The ignited mass is dissolved in water, and for the purpose of determining the quantity of chloride of magnesium that may have been decomposed by the ignition, the percentage of chloride is determined by titration. The difference in the contents of chlorine before and after ignition is subtracted from the loss in weight, after allowance has been made for the absorption of oxygen and for the loss of hydrogen: the balance is water. The results obtained are calculated in the following manner:—From the total amount of the sulphuric acid found, that portion is deducted which is combined with calcium as calcium sulphate, the balance of the sulphuric acid is divided into two equal parts, for the purpose of calculating the contents of potassium sulphate and magnesium sulphate, according to the molecular proportion in which these salts are present in kainit and in schoenit. If there is an excess of potash left uncombined with sulphuric acid, then it is in the form of chloride of potash, likewise the amount of magnesia, uncombined with sulphuric acid, is to be reckoned as chloride of magnesia. The result of this calculation will tell how much potash is in the form of kainit (K_2SO_4 , $MgSO_4$, $MgCl_2$ with $6H_2O$), and how much of it is in the form of schoenit (K_2SO_4 , $MgSO_4$ with $6H_2O$) and in the form of chloride of potash. The sodium is reckoned as chloride of sodium.

(3) In calculating the contents of potash, of chloride of potash, and of sulphate of potash, from the weighed potassium-platinum chloride, the factors 0.1928, 0.3056, and 0.3566 are used, assuming that the atomic weight of platinum is 197.18.

(4) The two methods which have been described under Nos. 1 and 2, and which are in common use in the Stassfurt potash industry, i.e., the so-called precipitation method and the oxalic acid method, give almost identical results. The first method, however, deserves preference on account of greater simplicity in cases where potash alone is to be determined. Finkner's method likewise gives results which agree well with the results obtained by the customary methods. It consists in evaporating the salt solution with a sufficient quantity of platinum chloride, without previously removing the sulphuric acid, reducing the potassium-platinum chloride, and weighing the metallic platinum.

The following are the results of comparative analyses, executed by order of the manufacturers of muriate of potash. The sample investigated was taken from a quantity of 86,948 cwts. of carnallite; the following are the results:—

1. After the precipitation method .. 22.02 p.c. KCl
2. After the oxalic acid method .. 22.03 " "
3. After Finkner's method .. 22.01 " "

In another sample from 75,582 cwts. carnallite the following results were obtained:—

1. After the precipitation method .. 17.88 per cent.
2. After the oxalic acid method .. 17.88 " "

* For the Association of Official Agricultural Chemists of the United States.

In a third sample from 97,435 cwts. of carnallite the contents of chloride of potassium were as follows:—

1. After the precipitation method .. 18.44 per cent
2. After the oxalic acid method .. 18.38 „

Another method of potash determination which is used in many agricultural experiment stations, among them the Royal Station at Hohenheim in Wurtemberg, consists in precipitating the sulphuric acid and alkali earths with barium oxide and ammonium carbonate, and potash with platinum chloride. The results obtained with this method are, according to our experience, very inaccurate, and always too low. This is explained by the fact that it is impossible to precipitate sulphuric acid without at the same time precipitating some of the potash, unless it be in an acid solution.

A separation of the alkali earths, if potash alone is to be determined, is superfluous, for the reason that calcium and magnesium-platinum chloride are soluble in 90 per cent alcohol even with more facility than sodium-platinum chloride.

(7) There is a method in use and recommended by the Association of Official Agricultural Chemists of the United States of North America, termed the Lindo-Gladding method, for analysis of potash salts, and which has been reported to us by Dr. B. von Herff, of Washington. We subjected this method to a thorough test in our laboratory; the results obtained do not agree with those obtained by our customary methods, nor do they agree among themselves, if repeated analyses of the same sample are made. Moreover, this method is considerably more troublesome and subject to more errors than the precipitation method. An average sample of a large cargo contained:—

1. After the Stassfurt method.	1. After the Lindo-Gladding method.
1. 12.92 per cent K_2O .	1. 13.47 per cent K_2O .
2. 12.97 „ „	2. 12.39 „ „
3. 12.94 „ „	3. 13.29 „ „

Likewise the results of repeated analyses of a sample from a large quantity of sulphate of potash gave, according to the precipitation method, 52.7 per cent potash, while three determinations after the Lindo-Gladding method gave 53.40 per cent, 53.03 per cent, and 53.61 per cent. These figures presented will amply demonstrate the unreliability of this method.

THE QUANTITATIVE DETERMINATION OF RUBIDIUM BY THE SPECTROSCOPE.*

By F. A. GOOCH and J. I. PHINNEY.

In a recent paper issued from this laboratory (Gooch and Hart, *Amer. Jour. Science*, xliii., p. 448), the possibility of determining small amounts of potassium quantitatively by means of the flame spectrum was demonstrated. The work which we are about to describe was performed in the endeavour to see how far similar methods might be applicable to the quantitative determination of rubidium. It was shown in the former work that hollow coils of platinum wire may be adjusted to hold definite amounts of liquid, and that, by taking care to plunge the coil while hot into the liquid and to remove it from the liquid with its axis inclined obliquely to the surface, it is possible to take up constant amounts through a long series of experiments. It thus becomes possible to bring definite amounts of any soluble substance into a flame to be viewed spectroscopically. The potassium salt best adapted to spectroscopic use proved to be the chloride, and it was found to be advantageous to dry the coils over a hot radiator before introducing them into the flame. A large

Muencke burner gave the best sort of flame, an ordinary single prism spectroscope provided with an adjustable slit (the width of which we were able to fix by closing it upon wires of known diameter), and an observing telescope movable so that different portions of the spectrum might be shut out at will, served sufficiently well for the work. The coils were made of No. 28 platinum wire (0.32 m.m. in diameter), wound in about thirty turns to a spiral 1 c.m. long by 2 m.m. in diameter and twisted together at the ends to form a long handle. With the apparatus described it was found possible, under the most favourable conditions, to recognise the characteristic red line of the potassium spectrum when only 1-1000 m.grm. of potassium, in the form of the chloride, was brought to the flame. It appeared, furthermore, that a comparison of the brightness of two spectra produced in close succession could be made with all the accuracy to be anticipated in photometric measurements, and that therefore by gradual dilutions and successive testings a solution of potassium chloride of unknown strength could be brought to the point of containing as much potassium to the coil-full (and so, of course, to the c.c. or any other chosen volume) as a standard solution of known strength. By noting the final volume to which such an unknown solution was brought in the process of equalising its spectrum with that of the standard, its total contents in potassium was determined. In this manner the strength of solutions of pure potassium chloride proved determinable with accuracy, but when the effect of intermixing pure sodium chloride with the potassium salt was studied, it transpired that the brilliance of the potassium spectrum was markedly increased by the presence of the sodium in the flame, the maximum increase, which amounted to twenty per cent, appearing when the ratio of sodium chloride to potassium reached 100 : 1. It was found, however, that the practical difficulty of determining potassium in presence of sodium could be largely overcome by taking the precaution to bring the test solution and the standard to apparent equality as regards the potassium line, then to bring the solutions to an equality in respect to the sodium line by addition of sodium chloride to the standard, and finally to readjust the volumes of test and standard until the potassium lines were again equal. The accuracy of the determination of the potassium is, however, in spite of the precaution, somewhat affected by the presence of sodium,—the error, though, sometimes falling as low as 1-10 m.grm. in 10 m.grms., rising occasionally to 1 m.grm. in 15 m.grms. With the excellent gravimetric method which we possess for the determination of potassium recourse would, naturally, never be taken to the spectroscopic method except in cases where small absolute amounts are concerned, but in such cases the spectroscopic method may prove a convenience.

In the work upon potassium the observations of the red line were made in the ordinary laboratory in diffused light, but preliminary experimentation upon the rubidium spectrum immediately developed the fact that the blue lines are better to work by in the case of this element, and that a dark room becomes a necessity. For the experiments to be described pure rubidium chloride was prepared by many fractional precipitations by alcohol out of aqueous solutions, and in settling the question as to the coils which should be used, the choice fell upon the size holding 0.02 grm. of water and made of the No. 28 wire, the superior stiffness of these and consequent constancy in capacity giving them the advantage over smaller coils of finer wire, though the latter are capable of bringing out greater sensitiveness of the reaction. We found, for example, that under the most favourable conditions as to height of flame and width of slit, 0.0002 m.grm. of rubidium chloride produced the blue lines at the last limit of visibility, when the larger and heavier coil was in the flame; with a coil holding 0.006 grm. of water and made of very fine wire, the more immediate volatilisation of the chloride so increased the delicacy of the spectroscopic reaction that it was possible to see the lines from 0.00005

* From the *American Journal of Science*, vol. xliiv., Nov., 1892.

m.-gm. of the salt. These figures serve as an indication of the possible delicacy of this method of producing spectra, but it should be remembered that all eyes do not see the rubidium lines with equal ease.

In experimenting with rubidium sulphate in place of the chloride, the lighter coil appeared to lose its advantage in point of delicacy of the indication over the larger coil, possibly because the amount of metal introduced into the flame has less influence upon the rate of vapourisation of the less volatile sulphate, and the lines of the sulphate appeared equally distinct and of longer duration than those of the chloride; but, while we judged the sulphate to be rather preferable in qualitative work, our earlier preliminary quantitative experiments led us to abandon it for the purposes of our investigation on account of the great uniformity in the lines yielded by the chloride. We found it desirable in comparative tests of brightness to employ as the standard the lines given by amounts of the chloride not exceeding 0.0005 m.-gm. to 0.0007 m.-gm., to set the slit at a width of 0.2 m.m., and to bring the coils to the flame in sets of three—the first, usually a standard, serving to fix the position of the lines so that the comparative distinctness of the lines given by the other two might be the more readily determined. The tables below contain the record of an attempt to dilute a solution of the pure chloride to the strength of the standard solution under the guidance of comparative tests of the brilliance of the spectral lines yielded by the residue left upon the wires after the evaporation of the solutions taken up by coils of equivalent capacity. Dilutions were made in ordinary graduated cylinders of suitable capacity.

Experiment I.

Standard. Rubidium in a coil-full (1.50 c.m. ³).	Test (known to contain 10 m.-gm. Rb.). Vol. in c.m. ³	Line of test compared with standard.
0.0005 m.-gm.	200	Brighter.
" "	300	"
" "	350	"
" "	370	"
" "	390	"
" "	400	{ Brighter (faintly).
" "	400	{ " " " " }
" "	400	{ Doubtful. " }
" "	410	{ Brighter (faintly).
" "	410	{ Weaker. " }
" "	420	{ Equally bright.
" "	420	{ Weaker. " }
" "	430	Invisible.

When the volume of the test solution reaches 400 c.m.³ the indications are, on the whole, that the solution is still stronger than an equal volume of the standard; and when the volume amounts to 420 c.m.³ it is safe to conclude from the indications that the test solution is the weaker. If the mean of the numbers representing these two volumes be taken as probably indicative of the volume at which the test and standard lines are at an equality, we have the estimated amount of rubidium in the test solution given by multiplying the volume in c.c. by the number of coil-fulls in 1 c.m.³, and the product by the amount of rubidium contained in a coil-full of the standard solution— $410 \times 50 \times 0.0005 = 10.25$ m.-gm. The amount of rubidium actually taken in the test solution was 10 m.-gm., and the error of the mean value assumed is 2.5 per cent +, between extremes corresponding to an error of 0 and 5 per cent +, respectively.

Experiment II.

Standard. Rubidium in a coil-full (1.50 c.m. ³).	Test (known to contain 10 m.-gm. Rb.). Vol. in c.m. ³	Line of test compared with standard.
0.0005 m.-gm.	340	Brighter.
" "	370	{ Equally bright.
" "	370	{ Brighter.
" "	390	{ Weaker.
" "	390	{ " " " " }

$$\text{Found } \frac{370 + 390}{2} \times 50 \times 0.0005 = 9.5 \text{ m.-gm.}$$

Taken 10.0 "
Error 0.5 " = 5 p.c.

Experiment III.

Standard. Rubidium in a coil-full (1.50 c.m. ³).	Test (known to contain 10 m.-gm. Rb.). Vol. in c.m. ³	Line of test compared with standard.
0.0005 m.-gm.	300	Brighter.
" "	360	{ Equally bright.
" "	380	{ Brighter.
" "	380	{ " " " " }
" "	390	{ " " " " }
" "	400	{ Weaker.
" "	410	{ " " " " }

$$\text{Found } \frac{390 + 400}{2} \times 50 \times 0.0005 = 9.875.$$

Taken 10.0 "
Error 0.125 = 1.25 p.c.

These results make it plain that when the comparison is made between solutions of pure rubidium chloride the spectroscopic method is capable of yielding fair approximations to truth. In the practical determination of rubidium, however, the question of the effect of the presence of sodium and potassium which naturally accompany it is of importance. Attention was therefore turned next to the consideration of this point, and the record of observations as to the influence of sodium upon the brightness of the rubidium spectrum is contained in the accompanying tabular statement.

Standard. Rubidium in a coil-full (1.50 c.m. ³) M.-gm.	Test solution. Sodium in a coil-full, M.-gm.	Comparison of lines of test by pairs.	Comparison of lines of test with standard.
0.00066	{ 0.00026 0.00260 }	{ Slightly brighter. Slightly fainter. }	Brighter.
"	{ 0.00130 0.00260 }	{ Equally bright.	Brighter.
"	{ 0.00260 0.00520 }	{ Equally bright.	Brighter.
"	{ 0.00260 0.00660 }	{ Brighter. Fainter. }	Brighter.
"	{ 0.00260 0.00780 }	{ Brighter. Fainter. }	Brighter.
"	{ 0.00260 0.01500 }	{ Brighter. Invisible on account of glare. }	Invisible.

(To be continued).

THE
ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 256).

In order to ascertain the comparative accuracy of the results obtained by means of the ordinary gravimetric methods, as compared with those obtained by means of the current, a series of experiments was made with the

Copper (Determined as CuO).

Copper formate taken in grms.	Copper by theory in grms.	Copper in CuO formed.	Difference in percentage from theoretical. Per cent.
1. 0.8024	0.2252	0.2261	+0.39
2. 0.7924	0.2226	0.2232	+0.27
3. 0.7063	0.1984	0.1982	-0.10
4. 0.7063	0.1984	0.1979	-0.25

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxix., No. 136.

metals chosen for particular study. The gravimetric method adopted was the same for all three, namely, estimation as oxide conducted in the ordinary way.

The first two determinations were high, due perhaps to the efflorescence of the salt. All subsequent weighings were done in a covered watch-glass, and the results obtained corresponded closely with the theoretical.

In the following electrolytic depositions of copper, solutions of copper formate of known strength were used.

Copper (Determined Electrolytically).

Copper present in solution.	Copper found.	Free formic acid.	C.c. H ₂ O.	Time in hours.	Difference in percentage from theoretical.
Grams.		C.c.			Per cent.
1. 0.1434	0.1438	10	125	46	+0.27
2. 0.1074	0.1075	15	125	16	+0.09
3. 0.0987	0.0988	5	125	17	+0.10
4. 0.0987	0.0987	10	125	16	0.00
5. 0.1074	0.1077	10	125	16	+0.27
6. 0.1057	0.1056	10	125	17	-0.09
7. 0.1057	0.1052	15	125	17	-0.47
8. 0.1101	0.1104	10	125	42	+0.27

In the above experiments a platinum dish was used at the negative pole, and the wire spiral as the anode. A current of 0.8 to 1.60 c.c. HO gas per minute was allowed to run over night. The poles were separated 2.5 c.m. Before cutting off the current the level of the liquid in the dish was raised by the addition of water, and the current allowed to act for an additional half hour. No further deposit of copper took place on the clean surface of the dish, indicating that the metal was completely precipitated. The current was then discontinued, the liquid quickly poured off, and the dish washed with hot water, being finally dried on a warm iron plate at a temperature not exceeding 100° C. The dish was then set aside for some time until it had acquired the temperature of the room and weighed. The solutions failed to give any indication, except the merest traces, of copper when tested with ferrocyanide of potassium. The time varied from sixteen to forty-six hours without materially affecting the result. No perceptible oxidation took place during drying, although the deposit was somewhat dark. It came out as a compact adherent coating, readily dissolving in nitric acid.

A comparison between the results obtained shows conclusively not only that the deposition of copper from its formate solution can be accomplished, but that it is fully as accurate as the ordinary gravimetric method.

Zinc (Determined as ZnO).

Zinc formate taken in grams.	Zinc by theory in grams.	Zinc in zinc oxide found.	Difference in percentage from theoretical.
			Per cent.
1. 0.5508	0.1875	0.1870	-0.26
2. 0.5508	0.1875	0.1876	+0.05
3. 0.5508	0.1875	0.1869	-0.31
4. 0.5508	0.1875	0.1872	-0.16

The four determinations made by the usual gravimetric method were estimated finally as zinc oxide, which, for purposes of comparison, have been converted into metal.

Zinc (Determined Electrolytically).

Zinc present in grams.	Zinc found.	Free acid.	C.c. H ₂ O.	Time in hours.	Current in HO gas per minute.	Difference in percentage from theory.
		C.c.			C.c.	Per cent.
1. 0.0625	0.0614	none	100	16	1.8	—
2. 0.0625	—	10	100	16	1.8	—
3. 0.1250	—	15	100	16	2.0	—
4. 0.0818	0.0476	5	100	17	0.8	—
5. 0.0818	0.0816	15	100	17	1.7	-0.24
6. 0.0818	0.0819	15	100	16	1.7	+0.12
7. 0.0513	0.0513	25	100	16	1.7	—
8. 0.1026	0.1021	10	100	17	1.7	-0.48
9. 0.1026	0.1023	15	100	43	1.8	-0.29
10. 0.1006	0.1007	10	100	16	1.7	+0.09
11. 0.1006	0.1003	10	100	16	1.7	-0.29

The foregoing determinations of zinc formate were performed under a variety of conditions. 1, 2, 3, 4 were made with the dish as cathode and the wire spiral as the positive pole; the results, both with and without free acid, were unsatisfactory, the deposit being very spongy and failing to come out completely, as proved by testing the solution with potassium ferrocyanide. The dish was then made the anode, and the zinc was allowed to separate on the platinum crucible, which was made the negative pole. The amount of free acid varied from 10 to 25 c.c. The deposit was grey and adherent on the sides and bottom, but rather spongy at the periphery. Around the top of the crucible the metal was black in colour. The final determinations were accurate, but required the greatest care to avoid detaching loose particles of metal.

The deposit was not regular, the bottom of the crucible being more or less free from zinc on account of the accumulation of gas. The time of deposition averaged sixteen hours. Such currents as sufficed to separate copper were unsatisfactory, even when the electrodes were brought in close contact. In the determinations that were satisfactory, the current strength varied from 1.6 to 1.8 HO gas per minute, and the poles were close together.

Cadmium (Determined as CdO).

Cadmium formate taken.	Cadmium by theory.	Cadmium in CdO found.	Difference in percentage from theory.
			Per cent.
1. 0.4224	0.1988	0.1983	-0.25
2. 0.4224	0.1988	0.1982	-0.30

Both results are somewhat too low, possibly owing to reduction of the oxide to metal and consequent loss by volatilisation.

Cadmium (Determined Electrolytically).

Cadmium present in grams.	Cadmium found in grams.	Free acid.	C.c. H ₂ O.	Time in hours.	Difference in percentage from theoretical.
		C.c.			Per cent.
1. 0.0497	0.0498	15	100	16	+0.20
2. 0.0994	0.0996	10	100	18	+0.20
3. 0.0994	0.0991	10	100	16	-0.30
4. 0.1231	0.1228	10	100	44	-0.40
5. 0.1231	0.1229	10	100	17	-0.16
6. 0.0984	0.0984	10	100	16	—
7. 0.0984	0.0985	10	100	16	+0.10
8. 0.1004	0.1005	10	100	16	+0.09
9. 0.1004	0.1002	10	100	17	-0.19

The dish was used as the negative electrode, the spiral as the positive, except 1, in which the cadmium was deposited on the crucible, the dish serving as the anode. The distance between the poles was 2.5 c.m. The variations in the conditions of the experiments noted above caused no noticeable difference in the results. The deposit was not apparently oxidised by moderate warming. Current 1.25 to 1.5 c.c. HO gas per minute.

The solutions were tested for cadmium at the conclusion of each experiment, but none was found, proving that the metal was completely deposited. It formed a firm and adherent coating, white in colour, with a bright metallic lustre.

I. Influence of Dilution upon the Precipitation of Copper.

Copper present in grams.	Copper found.	Free acid.	C.c. H ₂ O.	C.c. HO gas per minute.	Time in hours.
		Drops.			
1. 0.0717	0.0199	3	100	1.75	1
2. 0.0358	0.0111	10	100	1.75	1
3. 0.0179	0.0057	10	100	1.75	1
4. 0.0089	0.0028	10	100	1.75	1
5. 0.0044	0.0014	10	100	1.75	1
6. 0.0022	0.0006	10	100	1.75	1
7. 0.0011	0.0002	10	100	1.75	1

The distance between the poles was 2.5 c.m. The area of the electrodes was (3.8 c.m. × 3.17 c.m.) × 2. The

deposition was performed in beakers having a capacity of 400 c.c., a height of 10 c.m., and 7.6 c.m. in diameter. The deposit was bright and adherent, and, although the amount of free acid present was very small, the metal was not spongy. The results obtained were in close accord with those assigned by theory, according to the law that the amount of metal deposited in a given time is proportional to the strength of solution.

II. The Influence of Temperature upon the Precipitation of Copper.

	Copper taken in grms.	Copper deposited.	Free acid.	C.c. H ₂ O.	Time in hours.	Temperature in degrees Cent.
1.	0.0211	0.0019	none	150	1	20°
2.	0.0211	0.0046	"	150	1	40°
3.	0.0211	0.0080	"	150	1	60°
4.	0.0211	0.0119	"	150	1	80°

The area of the electrodes was (3.5 c.m. × 3.8 c.m.) × 2. Distance between poles 2.8 c.m. The current gave 1.25 c.c. HO gas per minute. 1 was slightly spongy, and had a slight deposit of basic green salt at the top. 3 was somewhat dark and slightly spongy at the top, but adherent. The amount of metal deposited increased with rise of temperature as follows:—0.0027 gm. (20°—40°), 0.0034 gm. (40°—60°), 0.0039 gm. (60°—80°). The ratio of increase also rose with the temperature, being greatest between 60° and 80°. In the above series the determinations were made in neutral solutions; in the following, 15 c.c. of formic acid was added.

	Copper taken. Grms.	Copper deposited. Grms.	Free acid. C.c.	H ₂ O. C.c.	Time. Hours.	Temperature in degrees Cent.
1.	0.1057	0.0104	15	150	½	20°
2.	0.1057	0.0164	15	150	½	40°
3.	0.1057	0.0237	15	150	½	60°
4.	0.1057	0.0319	15	150	½	80°

The distance between the poles was 2.9 c.m., area of electrodes (3.5 c.m. × 3.8 c.m.) × 2, current strength 7.5 c.c. OH gas per minute. The ratio of increase was:—(20°—40°) 0.0060 gm., (40°—60°) 0.0073 gm., (60°—80°) 0.0082 gm. A comparison between the two series of results would indicate that the presence of dilute free acid in moderate quantity exercises no material influence on the amount of metal deposited, even at elevated temperatures.

III. The Influence of Pole Separation upon the Precipitation of Copper.

	Copper taken. Grms.	Copper deposited. Grms.	H ₂ O. C.c.	Time. Hours.	Distance between electrodes. C.m.
1.	0.1974	0.0133	700	1	1.58
2.	0.1974	0.0106	700	1	3.16
3.	0.1974	0.0093	700	1	4.75
4.	0.1974	0.0084	700	1	6.33
5.	0.1974	0.0078	700	1	7.91
6.	0.1974	0.0073	700	1	9.50
7.	0.1974	0.0064	700	1	12.66

The area of the electrodes was (3.8 c.m. × 3.48 c.m.) × 2, free acid pressure 10 c.c. 1 was slightly spongy. 7 was very close to the edge of the dish. The diminution was 1—2 0.0027 gm., 2—3 0.0013 gm., 3—4 0.0009 gm., 4—5 0.0006 gm., 5—6 0.0005 gm. The current gave 1.75 c.c. OH gas per minute.

The foregoing experiments were performed in a crystallising dish 15.2 c.m. by 7.6 c.m., with a capacity of 900 c.c. In the following series the determinations took place in a beaker 10 c.m. in height by 7.6 c.m. in diameter.

The current gave 1.75 c.c. oxyhydrogen gas per minute, area of electrodes (3.8 c.m. × 3.16 c.m.) × 2, free acid present 5 c.c. The diminution was:—1—2 0.0054 gm., 2—3 0.0040 gm., 3—4 0.0036 gm. In both series the rate of

	Copper taken. Grms.	Copper deposited. Grms.	H ₂ O. C.c.	Time. Hours.	Distance of electrodes. C.m.
1.	0.1434	0.0302	200	1	1.58
2.	0.1434	0.0248	200	1	3.16
3.	0.1434	0.0208	200	1	4.75
4.	0.1434	0.0172	200	1	6.33

diminution rapidly lessened as the distance between the electrodes increased.

Experiments made under conditions similar to the above, except that no free acid was present, were failures, the deposits being exceedingly spongy.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 11th, 1892.

MR. WALTER BAILY, M.A., Vice-President, in the Chair.

MR. PORTER was elected a member of the Society.

The Discussion on Mr. Williams's paper, "*The Dimensions of Physical Quantities*," was resumed by Dr. BURTON.

He remarked that the idea that so-called "specific quantities," such as specific gravity, are pure numbers, was an erroneous one, and liable to lead to difficulties. The specific gravity of a substance was of the nature of density, and was only a simple number on the convention that the density of water was taken as unity. If dimensions be given to specific quantities, their interpretation would, he thought, be easy when the rational dimensional formulæ were found.

Referring to prof. Fitzgerald's comments, he said that although the contention that all energy is ultimately kinetic could not be gainsaid, the distinction commonly drawn between kinetic and potential energy involved nothing contrary to this view and was useful and convenient in many cases. As to the dimensions of μ and k , he was inclined to favour Mr. Williams's views, for several considerations suggest that the two capacities of the medium are essentially different. Arguments to show that μ was probably absolutely constant in the ether, whilst k might be variable, were brought forward. Of the two systems of dimensions for μ and k suggested by Mr. Williams, that which made μ a density seemed preferable.

Prof. A. LODGE said he was greatly interested in propagating the idea that physical quantities are concrete, and therefore welcomed Mr. Williams's paper. He thought it desirable to keep some names for abstract numbers, and "specific gravity" should be one. If another name involving dimensions was required, "specific weight" or "weight per unit volume" might be used. Speaking of the dimensions of the various terms of an equation, he did not think it was usually recognised that in ordinary algebra or Cartesian geometry the principle of directed terms was rigidly adhered to; for, if directed at all, every term of such an equation was directed along the same line. In this respect ordinary algebra was more rigid than vector algebra. Even if circular functions were involved, as in polar co-ordinates, they had the effect of making the directions of the terms the same. Other instances of problems bringing out the same fact were mentioned.

Mr. BOYS thought Mr. Madden had been arguing in a circle when he spoke of the astronomical unit of mass and deduced the dimensions of mass as L^3/T^2 from the equation $MLT^{-2} = M^2/L^2$, for it was quite impossible that this equation could be true unless γ (the gravitation constant) was introduced on the right-hand side. Mr.

Williams's method was quite the reverse; for he maintained that unless k and μ were introduced in the dimensions of electric and magnetic quantities, their dimensional formulæ could not indicate the true nature of those quantities, and hence were open to objection.

Mr. W. BAILY, whilst agreeing with Mr. Williams on most essential points, thought the total omission of L from dimensional formulæ made the expressions more complicated and less symmetrical. For example, such expressions as XY/Z , X^2 , and XYZ , which respectively represented undirected length, area, and volume, might with advantage be written L , L^2 , and L^3 respectively. The restriction of the dimensions of μ and k to those which give interpretable dimensional formulæ for electrical and magnetic quantities seemed scarcely justified. Both the systems proposed could not be right, and he thought it would be more in accordance with our present want of knowledge if a quantity, U , of unknown dimensions were introduced, such that μ or $k = U \cdot \text{density}$, and k^{-1} or $\mu^{-1} = U \cdot \text{rigidity}$. This would keep in view the fact that the absolute dimensions of quantities involving U were unknown. A list of the dimensions of the various quantities based on this arrangement was given.

Mr. SWINBURNE, referring to the conventional nature of many units, said great differences exist between the ideas held by different persons about such units. Starting with the convention that unlike quantities could be multiplied together, he might have 6 amperes flowing in an electric circuit under a pressure of 10 volts, and he might say he had 60 volt-amperes. The term "volt-ampère" could be regarded as indicating that the 60 was the numerical result of multiplying a number of volts by a number of amperes, or on the other hand it might be understood as a new unit, a watt, compounded of a volt and an ampère. Before Prof. Rücker's paper on "Suppressed Dimensions" was published, an electrician might have suggested measuring the length of a bench by sending an alternating current through it and determining its self induction, which he regarded as a length. Prof. Rücker, however, would say that this could not give the right result, for μ must be taken into account. He was inclined to think that dimensions were liable to mislead.

Referring to scientific writers as authorities, he said Maxwell had been careless in some cases, for he had sometimes given dimensional formulæ as zero, which really ought to have been $L^0 M^0 T^0$, or unity. In French text-books the errors had been corrected.

Mr. WILLIAMS, in reply to Mr. Madden's remarks about self induction being a length, pointed out that the subject might be looked at in two different ways, depending on whether one thinks of the *standard* of self-induction as the practical standard of measurement, or the *unit* of self-induction as a physical quantity. In the former case, the *standard* was a length, but in the latter the *unit* was a quantity of the same *species* as self-induction, the nature of which was, as yet, unknown. If its dynamical nature was known, then the absolute dimensions of all other magnetic and electric quantities would also be determined.

In answer to Prof. Fitzgerald's remarks, he said it was hardly likely that he should be unacquainted with the common view that kinetic and potential energies were ultimately quantities of the same kind, for it was a view with which he was quite familiar. The fact that they have the same dimensions was sufficient to show their identity, and the idea that all energy is ultimately kinetic was fundamental to his paper. This, however, did not imply that electrification and magnetisation are of necessity the same, and the suggestion that they may be the same was only one of several "probable suggestions," all of which were entitled to consideration. His chief reason for regarding Prof. Fitzgerald's suggestion as probably incorrect, was that it led to a system of dimensional formulæ incapable of rational mechanical interpretation, and containing fractional powers of the fundamental

units. Prof. Fitzgerald's system would make resistance an abstract number, and μ and k directed quantities, whereas the former was a concrete quantity, the two latter must be scalar in isotropic media. If he (Mr. Williams) had erred in treating electrification and magnetisation as different phenomena, he could only plead that he had done nothing more than follow such authorities as Lord Kelvin, Dr. Lodge, and Mr. O. Heaviside in the matter.

The Discussion on Mr. Sutherland's paper "*The Laws of Molecular Force*," was re-opened by Prof. PERRY reading a communication from the President, Prof. FITZGERALD.

He objected to discontinuous theories, especially when Clausius had given a continuous formula much more accurate over a very long range than Mr. Sutherland's discontinuous one. The introduction of Brownian motions without carefully estimating the rates required and energy represented, and without giving any dynamical explanation of their existence, was not satisfactory. It would, he said, be most interesting if Mr. Sutherland would calculate the law of variation of temperature with height of a column of convectionless gas, under conduction alone (for Maxwell thought the inverse fifth power law of molecular attraction was the only one that gave uniformity of temperature under these conditions), and if necessary make tests with solid bars. Referring to the statement that molecular attraction at 1 c.m. was comparable with gravitation at the same distance, he thought Mr. Boys would question this, and he suggested an *experimentum crucis* of the inverse fourth power law. Both the inverse fourth and inverse fifth power laws assumed symmetry which did not exist. He also took exception to other parts of the paper.

Dr. GLADSTONE, referring to the relative dynic and refraction equivalents given in Table XXVIII. of the paper, said he thought it interesting to make a similar comparison between dynic and dispersion, and magnetic rotation equivalents. The result as exhibited in a complete table showed a certain proportionality between the four columns, but the differences were beyond the limits of experimental error. Mr. Sutherland, however, sometimes reckoned the dynic equivalent of hydrogen as 0.215 and at other times looked upon it as negligible. The analogies between the optical equivalents did not depend on the proportionality of the numbers so much as upon the fact that the refraction, dispersion, and magnetic rotation equivalents of a compound was the sum of the corresponding equivalents of its constituent atoms, modified to some extent by the way in which they were combined. Whilst a somewhat similar relation held true for the dynic equivalents, the effect of "double-linking" of carbon atoms, so evident in the optical properties, was scarcely perceptible. The result of calculating the constants from Ml instead of from $M^2 l$ was next discussed, the effect of which was to quite upset the proportionality before noticeable.

Mr. S. H. BURBURY said that on referring to the author's original paper on which the present one was based, he found that uniform distribution of molecules was assumed. On this supposition the demonstrations given were quite correct, and the potential was a maximum. If, however, the molecules were in motion, the average potential must be less than the maximum, and the deductions in the present paper being based on wrong assumptions were liable to error.

Prof. RAMSAY remarked that many statements in the paper on the subject of critical points were very doubtful. Separate equations for the different states of matter were not satisfactory, neither was the artificial division of substances into five classes. The predicted differences in the critical points due to capillarity had not been found to exist. Speaking of the virial equation, he said that hitherto R had been taken as constant. Considerations he had recently made led him to believe that R was

not constant. The whole question should be reconsidered regarding R as a variable.

Mr. MACFARLANE GRAY said he had been working at subjects similar to those dealt with in Mr. Sutherland's paper, but from an opposite point of view, no attraction being supposed to exist between molecules. In the theoretical treatment of steam he found that no arbitrary constants were required, for all could be determined thermodynamically. The calculated results were in perfect accord with M. Cailletet's exhaustive experiments except at very high pressures, and even here the theoretical volume was the mean between those obtained experimentally by Cailletet and Battelli respectively.

Prof. HERSCHEL pointed out that Villard's equation had discussed the equation of the virial, where the chemical and mechanical energies were not supposed to balance each other. Mr. Sutherland's paper all turns on the existence of such a balance, and he (Prof. Herschel) could not understand why this balancing was necessary.

The Discussion was then closed and the meeting adjourned.

NOTICES OF BOOKS.

Outlines of Organic Chemistry. By CLEMENT J. LEAPER, F.C.S. London: Iliffe and Son. Small 8vo., pp. 118.

WE had begun to hope that the stretch of elementary chemical treatises with which we have been inundated for so many years was beginning to abate; it seems we were mistaken. "Still they come," and the painful questions which they suggest remain without an answer. We know that if a man becomes really interested in any Science he requires in after life, perhaps, ten times as many books on the subject as he did when a pupil.

Now, as no such supply of advanced chemical works seems to be demanded, we can only conclude that of the multitudes who have attended chemical classes and been duly examined, a vast majority at once throw the study aside and in after life remain unaffected by what they have learnt. This fact,—a peculiarity, we believe, of Britain—might alone suffice to show that as far as higher education is concerned we are "on the wrong tack."

This little work before us is avowedly examinational, and of course duly "departmental."

The Pharmacy and Poison Laws of the United Kingdom. Their History and Interpretation. With a brief Account of the Pharmacy Laws in Force in Australasia, Canada, and Cape Colony. London: Office of the *Chemist and Druggist*. Melbourne: Office of the *Chemist and Druggist* of Australasia.

IF the poison and pharmacy laws of this country were free from inconsistency they would be grossly un-English. It seems almost farcical to hedge in the sale of "poisons" with complicated formalities, whilst the open sale of explosives, ammunition, and fire-arms is allowed to go on. This is the greater grievance, since the lawful and harmless uses of fire-arms are very limited, whilst the lawful and harmless uses of poisons in the arts and manufactures are almost innumerable.

We know that there are persons who seek for an extension of the present laws, and would even restrict the sale of the ordinary mineral acids to the chemists and druggists. Several attempts have been in fact made in this direction, but fortunately for the arts they have not been successful. The Council of the Pharmaceutical Society in 1882 made itself responsible for an attempt of this nature.

The work before us, it will be seen, is simply historical and declaratory. It neither criticises nor justifies the existing laws, nor does it advocate their alteration. It

will be very useful to all dealers in chemicals as explaining to them in clear language what articles they may sell and under what regulations.

Short Manual of Experimental Chemistry. By A. DUPRÉ, Ph.D., F.R.S., F.C.S., &c., and H. WILSON HAKE, Ph.D., F.C.S., &c. Second Edition, Revised. London: C. Griffin and Co., Limited.

THIS work is an exceedingly favourable specimen of—as we may call them—the intermediate class of chemical text-books. It is distinct, on the one hand, from the bald manuals whose existence we have so often had to regret, and, on the other hand, from the necessarily voluminous publications of Watts, or of Roscoe and Schorlemmer. Whilst useful as a class-book it may often be advantageously consulted as a work of reference. Among its many commendable features it is free from the taint of examinationism.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 19, November 7, 1892.

Honours to M. Pasteur.—The members of the Section of Medicine and Surgery have formed themselves into a committee to present some appropriate testimonial to M. Pasteur on the occasion of his reaching the age of 70 years, which will take place on December 27th.

The Influence of the Distribution of Manures in the Soil upon their Utilisation.—Th. Schloësing.—The author is studying the effects of a complete and uniform distribution of manures in the soil, a point which, he considers, has not met with due attention. As the three essential principles of manures he regards potash, nitrogen, and phosphoric acid. His results will be given in a future communication.

Note on M. Berthelot's Reply to his Paper of October 24th.—Th. Schloësing.—The author declines to reply to the personalities of M. Berthelot.

Attempt at a General Method of Chemical Synthesis.—Raoul Pictet.—(See p. 262).

The Rotatory Power of the Salts of the Diamines.—Albert Colson.—All the salts examined were deflected in the same direction as the generating acid. If we extend to stable salts the principle of the conservation of the molecular type, we understand that one and the same solvent without immediate action upon the acid or the salts will not alter the direction of the rotatory power. We shall consider it natural that the tartrates, e.g., are dextrorotatory in an aqueous solution like the generating acid, whilst the diacetyl tartrates are levorotatory under the same conditions and from the same cause.

Volumetric Determination of the Alkaloids.—E. Léger.—Referring to the claim of priority raised on this subject by Herr Harsten as against M. Barthe, the author claims the priority for himself on the evidence of a note published in the *Journ. Phys. Chemie*, vol. xi., p. 425 (1885), on the application of phenolphthalein to volumetric analysis.

The Fixation of Free Nitrogen in Plants.—Th. Schloësing, junr., and Em. Laurent.—The authors contend that whilst the lower plants are capable of fixing the free nitrogen of the atmosphere it remains in them after fixation, whilst the subjacent soil is not enriched. In their experiments the fixation was effected by a

mixture of mosses and algæ, doubtless accompanied by bacteria. Consequently the process is confined to the surface, instead of taking place, as according to M. Berthelot, in the lower beds of the soil.

Observations on the above Paper.—M. Duclaux.

Observations on the Foregoing Papers.—M. Berthelot.—This controversy promises to become tedious.

On γ -Achromoglobine—A New Respiratory Globuline.—Dr. A. B. Griffiths.—The author gives to this new globuline the remarkable formula $C_{724}H_{915}N_{194}SO_{183}$.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. vii. and viii., Nos. 17 and 18.

Action of Chlorine upon the Alcohols of the Fatty Series. Isobutylic Alcohol.—A. Brochet.—The author has obtained a chlorine derivative of isobutylic acid of the composition C_4H_7ClO . It is a colourless mobile liquid of a pungent but bitter taste. It burns with a sooty flame bordered with green. It is evidently an aldehyd. Its boiling-point is 90° , and its specific gravity = 1.053.

Derivatives of α -Naphthylacetylene and β -Naphthylacetylene.—J. A. Le Roy.—The author describes dinaphthyladiacetylene, naphthylpropionic acid. He further gives an account of the action of chlorine upon α -ethylnaphthalene, the formation of α -naphthylacetylene; the action of phosphorus perchloride upon β -methyl-naphthylketone; β -naphthylacetylene, and of its hydration.

Process of the Oxidation and Sulphonation of Organic Substances by Ammonium Bisulphate.—Marcel Lachaud and Ch. Lepierre.—On causing pure aniline to act upon the bisulphate and heating the mass for a sufficient time it darkens and becomes black. In this mass the authors have recognised and partially separated by dialysis a black amorphous body soluble in water but insoluble in alcohol, a violet and a blue substance. If the impure aniline of commerce is caused to react upon ammonium bisulphate it turns red at once; on continuing to heat it passes through violets and blues to black. An entire series of colours, probably novel, are thus formed between 200° and 350° . Some of them are soluble in amyl alcohol (acid or ammoniacal), such as the reds and the violets. The blues and the blacks are insoluble. Some of them are strongly fluorescent.

On Paradiethylbenzene.—H. Fournier.—The author has undertaken to study the bromo-derivatives of paradiethylbenzene in the lateral chains.

On Benzylpentaethylbenzene.—H. Fournier.—This substance, $C_{23}H_{32}$, boils without decomposition above 360° . It crystallises from alcohol in fine white needles, which melt at 88° – 89° . It is very soluble in benzene, even in the cold, in ether, and boiling alcohol; but it is very sparingly soluble in cold alcohol.

Specific Gravity of Silk.—Leo Vignon.—The author contends that the values obtained by M. de Chardonnet are too high, as his silks must have been more or less weighted with metallic elements.

Thermochemical Study of Certain Organic Substances with Mixed Functions.—Leo Vignon.—Not adapted for useful abstraction.

Revue Universelle des Mines et de la Metallurgie.

Vol. xix., No. 3, September 1892.

Transformation of the Ordinary Safety-lamp into a Sensitive Indicator of Fire-damp.—F. Clowes.—A paper communicated to the Royal Society.

Royal Institution. — Christmas Lectures. — Sir Robert Ball, F.R.S., will deliver a course of six lectures (adapted to a juvenile auditory) on "Astronomy," commencing on Tuesday, December 27.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Society of Arts, 8. (Cantor Lectures). "The Generation of Light from Coal-Gas," by Prof. Vivian B. Lewes. Medical, 8.30.

TUESDAY, 29th.—Institute of Civil Engineers, 8.

WEDNESDAY, 30th.—Society of Arts, 8. "The Copper Resources of the United States," by James Douglas. British Astronomical Association, 5. Royal, 4. (Anniversary).

THURSDAY, Dec. 1st.—Institute of Electrical Engineers, 8.

Geologists' Association, 8.

Quekett Club, 8.

Chemical Society, 8. "On the Formation of Orcinol and other Condensation Products from Dehydracetic Acid," by J. Norman Collie. "Isolation of Two Predicted Hydrates of Nitric Acid," by S. U. Pickering. "Anhydrous Oxalic Acid," by W. W. Fisher. "Observations on the Origin of Colour and of Fluorescence," by W. N. Hartley. "The Origin of Colour—Azobenzene," by H. E. Armstrong. "The Reduction Products of $\alpha\alpha'$ -Dimethyl- $\alpha\alpha'$ -Diacylpentane," by Dr. Kipping. "The Products of the Action of Sulphuric Acid on Camphor," by Drs. Armstrong and Kipping. "Methods of Showing the Spectra of Easily Volatile and their Salts, and of Separating their Spectra from those of the Alkaline Earths," by W. N. Hartley.

TO CORRESPONDENTS.

G. W. Blythe.—In exact work all gases should be dried, whether prepared with dilute or strong acid. When hydrochloric acid is used the gas should also be passed through an absorbent for this acid.

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THE CHEMICAL NEWS.

Vol. LXVI., No. 1723.

ON THE ACTION OF PHOSPHINE ON SELENIUM DIOXIDE.*

By SIR CHARLES A. CAMERON.

THE author has studied the action of dry phosphine gas on a solution of selenium dioxide in absolute alcohol. Complete absorption takes place, and a rich yellow precipitate appears. The attempts made to determine accurately the composition of the yellow compound failed owing to its instability, for it no sooner made its appearance than it began to turn red owing to separation of selenium. It was found to contain both phosphorus and selenium, but at each determination in different proportions. Attempts to retard decomposition by conducting the processes in such a way as to exclude atmospheric air, and to expose the yellow compound to low temperatures, proved of little use. It was found that the proportion of selenium thrown out of solution varied according to temperature, and to the rapidity with which the phosphine was transmitted through the alcoholic solution. The greater part of the selenium remained in the alcohol, and exercising a reducing action on the alcohol produced ethyl selenide, $(C_2H_5)_2Se$.

DETECTION OF GOLD IN DILUTE SOLUTIONS.

By T. K. ROSE, B.Sc.,
Assistant Assayer to the Royal Mint.

It is well known that if large quantities of boiling water are poured into a solution of stannous chloride, a yellowish white gelatinous precipitate of tin hydrate is obtained. If the water contains a little chloride of gold the precipitate is coloured red (purple of Cassius). A solution of one part of gold per million parts of water treated in this way gives a bright rose-coloured precipitate almost instantaneously in a small test-tube. One in four millions gives a paler colour easily detected in a test-tube if comparison is made with the precipitate caused by distilled water. For more dilute solutions a greater bulk of liquid is required, and the precipitation is best effected in beakers.

If 0.0000311 grm. gold (one-millionth of an oz. troy) is dissolved in 3.11 litres of water, and the solution, containing one part per hundred millions, is raised to boiling and poured suddenly into a large beaker containing 10 c.c. of a saturated solution of $SnCl_2$ in water acidulated by HCl so as to mix the two liquids as rapidly as possible, a bluish purple precipitate is obtained. This precipitate, when collected in a test-tube, differs markedly in colour from a precipitate obtained by pure water in the same way. There seems no reason why a still more dilute solution of gold should not yield a colour if precautions are taken to ensure the complete mixture of precipitant and solution.

Quantitative results based on comparison may also be obtained with care, as the precipitates are quite stable in water. The presence of NaCl (3 per cent), $CaSO_4$, KCl, KBr, NH_4Cl , a little free HCl, &c., or all of these, do not interfere with the reaction. The precipitate is soluble in ammonia and is re-precipitated, showing its original colour, on neutralising with HCl. Synthetically prepared

sea-water containing gold to the amount of one in twenty millions (three-quarters grain per ton) is equally sensitive, but the colour is in this case a blackish rather than a purple violet. I am proceeding to test real sea-water in the same way, though quantitative results cannot be expected, since Sonstadt states (CHEMICAL NEWS, xxvi., p. 159) that only a small portion of the gold present is precipitated by stannous chloride.

This modification of a very well-known test appears likely to be useful in chlorination mills, where it is often desirable to detect the presence of gold in liquids containing as little as 1 in 5,000,000. The most dilute solution that reacts if treated in the ordinary way by $SnCl_2$ is one per million (*vide* text books, *passim*), and then only after a lapse of some hours.

Royal Mint, Nov. 26, 1892.

A SIMPLE CHEMICAL EXPERIMENT.

By ALEXANDER JOHNSTONE.

As illustrating a lecture on oxygen or air, a strong solution of pyrogallol in KHO or NaHO is often exposed to the gas or the atmosphere to show its great power of absorbing free oxygen, and its instant change of colour when exposed to it. This experiment "tells better" if a clear colourless solution of alkaline pyrogallol be shown to the class before exposure to oxygen. This can be done very easily and quickly. Into a rather deep test-glass, such as is ordinarily used in lecture experiments, place some solid pyrogallol acid and then a little water, just enough to barely dissolve it. Next put a small handful of sodium carbonate into a flask and cover with HCl to drive the CO_2 off. Pour the CO_2 gas into the glass above the pyrogallol, and then add the KHO to the latter. The class will see that the alkaline solution below the CO_2 remains colourless. To show the change caused by the presence of O, pass the latter from a tube into the lower stratum of the CO_2 covering, or incline the glass so as to throw out the CO_2 and admit the air. The change will be instantaneous.

This experiment should also be of service in making evident to the eye the diffusion of gases—the heavier CO_2 —slowly mixing upwards with the air and the latter downwards with the CO_2 , as evinced by the assumption of colour by the pyrogallol, and the gradual deepening of the colouration as the diffusion progresses.

Queen Margaret's College, Glasgow,
Nov. 18, 1892.

ON THE ORIGIN OF THE VARIOUS COLOURS OF NITRIC ACID.

By L. MARCHLEWSKI, Ph.D.

It is well known that on adding a little water to fuming nitric acid of a brown tint it immediately assumes a green colour, which, on further addition of water, turns blue, and on still further dilution entirely disappears.

This phenomenon was explained by Péligot, who relied principally on the physical properties, especially the colouring powers of the oxides of nitrogen assumed to be present. The explanation is briefly this:—That brown fuming nitric acid owes its colour to the nitrogen tetroxide dissolved in it, which possess the well-known ruddy-brown colour; that the green acid contains a mixture of brown nitrogen tetroxide and blue nitrogen trioxide along with nitric acid, and lastly, that the blue solution contains a mixture of nitric acid and nitrous acid, the colour being due to the nitrogen trioxide present. Nothing further was stated concerning the condition of

* Abstract of a Paper presented to the Royal Dublin Society Nov. 16, 1892.

the oxides N_2O_4 and N_2O_3 ; i.e., it remained uncertain whether free N_2O_4 is to be regarded as existing in the solution as such, and whether N_2O_3 exists as the free oxide or the acid.

The last question could not be settled at that time, as nothing was definitely known as to the existence of a hydrate of nitrous acid. It appeared to me that the above explanation, which could only be regarded as an *à priori* one, was unsatisfactory and required confirmation by experiment.

I made a series of experiments, the first part of which was published in the *Berichte* of the German Chemical Society. This paper was critically discussed by Veley in the *CHEMICAL NEWS*, lvi., 175. His remarks place my researches on the subject of this paper in a false light. My original method of research was as follows (*Berichte*, xxiv., 3271).

A stream of carbon dioxide was passed through each of the differently coloured acids, and the oxides evolved absorbed in concentrated sulphuric acid. According to Lunge (*Ber.*, 1882, p. 438) nitrous anhydride is absorbed to form pure nitrososulphuric acid and nitrogen tetroxide to form a mixture of nitrososulphuric acid and nitric acid. The analysis of the nitrogenous bodies with regard to (a) the total nitrogen, and (b) the nitrogen existing as nitrous acid, by Lunge's excellent method, ("Alkali-maker's Pocket-Book," Lunge and Hurter), should give information with regard to the oxides evolved from the coloured acids, and thus, as I thought, furnish a clue to the cause of colouration.

Mr. Veley censures me for not having mentioned in my communication either the time during which CO_2 was allowed to act on the acids, or the temperature at which the experiments were carried out. He remarks on the absence of any statement with regard to drying the gases, as well as any attempt to check the results by examination of the decolourised acids. Moreover, he makes me state that Péligot's explanation should be set aside as absolutely incorrect.

I am driven to conclude from Mr. Veley's statements (1) that he has only read my first communication hurriedly; (2) that he has not read my second paper at all; and (3) that he suggests the carrying out of useless experiments. The method of research used in the first paper depends, as already mentioned, on the mechanical removal of oxides of nitrogen by means of a stream of carbon dioxide and the analysis of the nitroso bodies carried away and absorbed in sulphuric acid. I expressly mentioned that each acid was treated with carbon dioxide until completely decolourised. The time varied with the amount of acid to be decolourised; the determination of the duration of the experiment would then have no object. Concerning the temperature I expressed myself with sufficient precision on p. 3273 (*Berichte*, xxiv.), where the decolourisation is said to have taken place in the cold.

I did not incline to believe in any particular influence of the temperature on the reaction, because, according to Péligot's theory, the only colour-producing oxides are N_2O_4 and N_2O_3 , and by raising the temperature the first would only split up into two molecules of NO_2 , and the second into NO_2 and NO , which latter behave exactly like nitrous acid in the presence of sulphuric acid. A rise of temperature would then cause absolutely no change in the analytical result except for the possible volatilisation of nitric acids. The CO_2 must obviously be dried before using, for a dilution of the prepared acid would alter its composition.

It is evident that the gas after passing through the coloured acid will be charged with water vapour, as well as with oxides of nitrogen; this circumstance can, however, have no influence on the analysis, as the amount of dilution necessary to decompose the nitrous acids is not nearly reached.

The result of my first research was to prove that the analytical methods used by me showed no difference in the composition of the green and blue acids, I observed

at the same time (*Berichte*, xxiv., p. 3275) that nitric oxide appears along with the higher oxides, and promised to report further on the occurrence of this gas.

By the prosecution of this question I became convinced that the analytical method which I had originally used was inadequate; that the nitric oxide observed was not necessarily present as such or in loose combination with other bodies, but that it can also be formed by the spontaneous decomposition of an aqueous solution of nitrous acid.

Montemartini (*Zeit. Physik. Chemie*, 1891, p. 93), maintained that this decomposition proceeds according to the differential equation for chemical reactions of the first order, and further, although this requires confirmation, that the rate of decomposition of nitrous acid, in presence of nitric acid, diminishes with increased concentration of the latter (*Atti Della Reale Accad. dei Lincei Redic.*, i., p. 63—67).

My supposition has been confirmed (*Zeit. Anorgan. Chemie*, i., p. 374); it can be proved that a stream of CO_2 passed through an aqueous solution of nitrous acid carries off a considerable quantity of nitric oxide. The problem as to the constitution of the coloured acids could not, therefore, be carried out in the way described. If the nitric oxide is produced by the splitting up of nitrous acid it masks the fact—thanks to its property of reacting with nitrogen tetroxide in the presence of sulphuric acid in the same way that N_2O_3 does.

If, on the contrary, nitric oxide is generated from some other source, or really does play a chemical part in the colouration of the acids, my earlier experiments would not prove decisive when placed alongside experiments instituted with aqueous solutions of nitrous acid. Consequently I felt justified in my second communication (*Zeit. Anorgan. Chemie*, i., 377) in drawing the conclusion that the physical theory completely expresses all the facts known; for I proved (1) that in the most highly concentrated fuming nitric acid of a brown colour, only nitrogen tetroxide exists along with nitric acid, and (2) that by dilution of such acid with ice-cold water, no loss of nitric oxide took place.

Now since, as is generally known, N_2O_4 can only split up into nitrous and nitric acids by the action of either water, sulphuric acid, or the alkalies, we must conclude that the mixture formed by dilution of brown fuming nitric acid can only contain HNO_3 , N_2O_3 , and N_2O_4 (the green acids), or HNO_3 and N_2O_3 (the blue acids).

The imputation that I deny Péligot's views is, then, entirely unfounded. I do not, of course, assume that N_2O_4 exists as such in the brown acid, I believe that I have furnished more reasons for the assumption that it combines chemically with the nitric acid (*Zeit. Anorgan. Chemie*, i., p. 380). The form in which N_2O_3 exists in the blue solution is quite unknown; we cannot unfortunately adopt any definite view with regard to it, since it has never been proved what the blue aqueous solutions of N_2O_3 may represent, whether they are simply solutions of N_2O_3 , i.e., N_2O_3 molecules distributed through a definite space by means of the solvent medium, or whether they are solutions of the hydrate HNO_2 .

I attacked this question, narrowed by the following consideration:—If N_2O_3 is present as such in an aqueous solution, the solution cannot be a conductor of electricity; if it is a conductor a decomposition must take place, and this would consist in the formation of the ions H and NOO (as $2NO$ and O). The necessary experiments were, however, so surrounded with difficulties that they gave somewhat indefinite results, and I determined not to publish them.

Mr. Veley censures me, lastly, for not having analysed the residual acids. That, as a matter of fact, I did not do, and why? In a third article (*Zeit. Anorgan. Chemie*, ii., p. 18), called forth by a research of Montemartini (*Atti Della Reale Accad. Lincei Redic.*, i., 63—67), I proved that a combination of the analysis of the gases evolved, with the analysis of the residual acids, can only

lead to illusory results, against which I wished to guard myself.

There is, unfortunately, no exact quantitative method of separating the oxides NO , N_2O_3 , and N_2O_4 , and nitric acid when all are present in the same solution.

The general results of all considerations lead more and more to the conviction that, so long as the chemistry of the individual oxides of nitrogen makes no further progress, it will remain impossible to find a direct experimental solution to the question of the constitution of blue and green nitric acids.

Every criticism of my work is welcome, particularly when it concerns such an extremely difficult subject as the chemistry of the oxides of nitrogen. They must, however, fulfil one condition: the critic must not pick out a single contribution—not even the first one—expressly designated as an introduction, and treat it alone to a close inspection.

The critic should rather have before him the whole of the work done in that province by the person criticised, and if he be an inorganic chemist he should not overlook a journal which is entirely devoted to inorganic chemistry, viz., "Die Zeitschrift für Anorganische Chemie von Kruss." These conditions Mr. Veley has not fulfilled.

Dr. Schunck's Laboratory,
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ATTEMPT AT A GENERAL METHOD OF CHEMICAL SYNTHESIS.

By RAOUL PICTET.

THE first point which we have had to verify experimentally in order to prove the agreement of our fundamental hypothesis with facts, consists in demonstrating that at very low temperatures all chemical reaction ceases. We have made more than two hundred experiments to this end, in which we have brought in contact the substances which react most energetically, those whose reactions are the most conspicuous, and those, lastly, which are in the liquid state notwithstanding the greatest cold.

We relate here only some of these observations:—

1. Concentrated sulphuric acid at 89 per cent, and that with ten molecules of water, having 35 per cent, yield two liquids, the congealing points of which are -56° for the former and 88° for the latter.

We put at -125° congealed sulphuric acid in contact with caustic soda finely pulverised and likewise refrigerated to -125° in a capsule. On strongly compressing the acid into the powder of caustic soda there appeared no reaction.

We then introduced into the refrigerating tank two insulated tubes, between which we caused the spark of a powerful Ruhmkorff's coil to strike over. We found that the frozen sulphuric acid conducted the spark very well, and after a quarter of an hour's operation we saw that the reaction of the acid upon the alkali was effected on the paths of the sparks, but without extending to the adjoining parts. The weight of sodium sulphate is thus relatively trifling, and this product is sprinkled over the surface of the column of frozen sulphuric acid. The temperature shown by the thermometer in the centre of this column of frozen acid, at the end of fifteen minutes is -121° , whilst the contents of the refrigerating tank were kept at -145° . These facts having been established, we withdrew the tube from the refrigerating tank, so as to allow the temperature to rise gradually. About -80° the reaction suddenly took place in mass, breaking the tube in consequence of the abrupt change of temperature.

Dilute sulphuric acid at 31 per cent behaved exactly in the same manner.

2. Sulphuric Acid and Caustic Potassa.—The operation was effected exactly in the same manner as with soda,

and gave the same results, only the reaction in mass took place already at -90° .

3. Sulphuric Acid and Concentrated Ammonia.—No reaction above -80° . A limited reaction under the influence of the electric spark, then at -65° or -60° a reaction in mass with a sudden rise of temperature.

4. Sulphuric Acid and Sodium Chloride.—No reaction below -50° ; from -50° to -25° limited reaction; then above, a reaction in mass.

5. Sulphuric Acid and Calcium Sodium Carbonates.—Taking sulphuric acid at 35 per cent liquid at -80° , no reaction with these two carbonates. The first bubbles of carbonic acid were liberated only at -56° for sodium carbonate and at -52° for calcium carbonate. At -15° with marble, and at -30° with sodium carbonate the action is turbulent. All other carbonates behave essentially in the same manner.

6. Nitric Acid with the same Substances as with Sulphuric Acid.—The acid is cooled down to -125° , as well as all the substances with which it is brought into contact. With caustic potassa and soda the reactions are at first null, but they are developed some degrees lower than with sulphuric acid if the temperature is allowed to rise gradually outside the tank.

With sodium chloride the reaction begins already at -74° with the aid of the spark.

7. Metallic Sodium at 84 per Cent.—The alcohol is cooled down (liquid) to -78° with the sodium. If the sodium is thrown into the alcohol there is no reaction. It begins only about -48° , and is suddenly developed in mass.

8. Sodium and Sulphuric Acid at 35 per Cent.—Both cooled down to -85° and brought into contact—no reaction. About -50° the reaction appears suddenly with flames. Below -50° sodium in contact with the acid retains its metallic lustre, as it does in dilute alcohol.

9. Potassium acts like sodium; at -68° (instead of -50°) it spontaneously ignites the hydrogen liberated by the sulphuric acid at 35 per cent ($\text{SO}_4\text{H}_2 + 10\text{H}_2\text{O}$).

10. We have made some experiments on reactions which yield solid precipitates.

Sulphuric Acid and Barium Chloride.—We refrigerate separately sulphuric acid at -85° and a solution of barium chloride in alcohol. We mix the two liquids, adding a few crystals of barium chloride. No reaction can be perceived and the sulphuric acid remains transparent. The precipitate only appears at -70° . At -40° the reaction is complete.

Hydrochloric Acid and Silver Nitrate.—An alcoholic solution of silver nitrate is cooled to -125° , as is also hydrochloric acid at 33 per cent. On mixing the liquids there is seen no deposit or turbidity. At -90° the reaction appears slightly, and it is complete at -80° .

11. Caustic Potassa and Phenolphthalein.—The potassa is dissolved in alcohol and the phenolphthalein likewise. They are cooled separately down to -135° , the paste state. On mixing there is no reaction. The temperature is allowed to rise, and at -100° the red tint appears, and at -80° the colour is intense.

Litmus with Sulphuric Acid and Hydrochloric Acid.—An alcoholic solution of litmus is cooled down to -140° , and poured either into frozen sulphuric acid or upon liquid hydrochloric acid at -125° . The solution remains blue indefinitely at -120° in spite of frequent agitation. At -110° the solution suddenly turns red with hydrochloric acid, and at -105° with sulphuric acid.

Summary.

We may sum up as follows the researches made in this direction:—

1. At the temperatures comprised between -155° and -125° we have not been able to recognise any chemical reaction whatever were the bodies brought into contact.

2. The visible reactions, such as the effect of acids upon tincture of litmus, &c., are produced at lower tempera-

tures than other very energetic reactions, such, e.g., as that of metallic sodium upon sulphuric acid.

3. In all chemical reactions we may find two phases, according to the temperature at which we operate.

A. The *slow reaction* which is produced below a certain limit of temperature which is special for the substances brought into contact. This reaction is manifested under the influence of the electric spark, according to the distance between the actual temperature and such limit of temperature.

B. The *reaction in mass*, in which the rise of temperature produced by the portions which react communicates to the adjacent parts heat enough to make them react.

In most cases to obtain and keep up the slow reaction, we must remove by radiation the heat developed by the combination; otherwise the temperature very quickly reaches the limit of the *reaction in mass*.

4. The electric spark seems to be the best excitant to provoke *slow reaction*.

It is therefore experimentally shown that every chemical reaction always commences with a *period of negative energy*, in which work must be supplied to the components from without, to permit their combination. The chemical work, called by M. Berthelot preliminary or preparatory, is therefore a general fact in nature.—*Comptes Rendus*, cxv., p. 814.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 267).

I. Influence of Dilution upon the Precipitation of Cadmium.

	Cadmium taken.	Cadmium deposited.	H ₂ O.	Free acid.	H ₂ O gas per minute.	OH gas per minute.
	Grm.	Grm.	C.c.	C.c.	Hours.	C.c.
1.	0.0994	—	100	none	$\frac{1}{2}$	1.75
2.	0.0497	—	100	"	$\frac{1}{2}$	1.75
3.	0.0994	—	100	0.5	$\frac{1}{2}$	1.75
4.	0.0994	0.0218	100	5	I	1.75
5.	0.0497	0.0109	100	$\frac{5}{2}$	I	1.75
6.	0.0248	0.0053	100	$\frac{5}{2}$	I	1.75
7.	0.0124	0.0026	100	$\frac{5}{2}$	I	1.75
8.	0.0062	0.0011	100	$\frac{5}{2}$	I	1.75

In 1 and 2 no free acid was added, and in 3 only 0.5 c.c. was present; all three were failures. The amount of acid was then increased to 5 c.c. and the experiment repeated, all the other conditions remaining the same. The deposit was adherent and compact. The poles were 3.16 c.m. apart, and had an area of (2.85 c.m. $\times$ 3.8 c.m.) $\times$ 2.

II. Influence of Temperature upon the Precipitation of Cadmium.

	Cadmium taken.	Cadmium found.	H ₂ O.	Free acid.	H ₂ O gas per minute.	Temperature in deg. C.
	Grm.	Grm.	C.c.	C.c.	C.c.	
1.	0.1231	0.0240	150	10	1.75	20°
2.	0.1231	—	150	10	1.75	40°
3.	0.0497	0.0088	145	25	1.75	20°
4.	0.0497	0.0110	145	25	1.75	40°
5.	0.0497	0.0210	145	25	1.75	60°
6.	0.0497	0.0257	145	25	1.75	80°

2 was very spongy, and was covered with a white gelatinous deposit resembling cadmium hydrate. The amount of cadmium was then diminished more than half, while the amount of formic acid present was increased to 25 c.c. 5 and 6 were somewhat spongy, but adherent. The increase was:—20°—40° 0.0022 grm., 40°—60° 0.0100

grm., 60°—80° 0.0047 grm. The amount of metal deposited increased with rise of temperature, being greatest at 80°, but the greatest ratio of increase was at 60°, being almost five times greater than at 40°, and more than twice as great as at 80°. These results were so different from those obtained with copper that a second series of determinations was made, in which the amount of cadmium in the solution was reduced still more in order to ensure a compact deposit at the higher temperatures. The results, which were in close accord with those above, are as follows:—

	Cadmium taken.	Cadmium deposited.	H ₂ O.	Free acid.	OH gas per minute.	Temperature in deg. C.
	Grm.	Grm.	C.c.	C.c.	C.c.	
1.	0.0193	0.0022	135	15	1.25	20°
2.	0.0193	0.0031	135	15	1.25	40°
3.	0.0193	0.0078	135	15	1.25	60°
4.	0.0193	0.0102	135	15	1.25	80°

III. The Influence of Pole Separation upon the Precipitation of Cadmium.

	Cadmium present.	Cadmium deposited.	H ₂ O.	OH gas per minute.	Separation of electrodes.
	Grm.	Grm.	C.c.	C.c.	C.m.
1.	0.0994	—	700	2.2	1.58
2.	0.0994	0.0059	700	1.25	1.58
3.	0.0994	0.0023	700	0.8	1.58
4.	0.0994	0.0009	700	0.8	3.16
5.	0.0994	0.0002	700	0.8	6.33
6.	0.0994	—	700	0.8	12.65

Although 20 c.c. of free formic acid was present in 1 and 2, both were failures, the latter, though it was weighed, being merely approximate, some particles having been washed off. The current was then reduced to 0.8 c.c. HO gas per minute. Adherent deposits were obtained, but in such small quantity that 5 yielded only a trace. The ratio of diminution was:—3—4 0.0014 grm., 4—5 0.0007 grm. Area of electrodes (3.8 c.m. $\times$ 3.48 c.m.) $\times$ 2, time one hour, free acid present present 10 c.c.

I. Influence of Dilution upon the Precipitation of Zinc.

	Zinc present.	Zinc deposited.	H ₂ O.	Free acid.	OH gas per minute.
	Grm.	Grm.	C.c.	C.c.	C.c.
1.	0.1250	0.0300	100	0.5	1.75
2.	0.0625	0.0155	100	0.25	1.75
3.	0.1250	0.0173	100	5	1.75
4.	0.0625	0.0083	100	$\frac{5}{2}$	1.75
5.	0.0313	0.0043	100	$\frac{5}{2}$	1.75
6.	0.0156	0.0028	100	$\frac{5}{2}$	1.75

1, 2, 5, and 6 were spongy, especially the last. Distance between the poles 3.16 c.m. Area (2.85 c.m. $\times$ 3.8 c.m.) $\times$ 2, time one hour.

II. Influence of Temperature upon the Precipitation of Zinc.

	Zinc taken.	Zinc deposited.	H ₂ O.	Free acid.	OH gas per minute.	Temperature in deg. C.
	Grm.	Grm.	C.c.	C.c.	C.c.	
1.	0.1539	—	150	10	0.3	20°
2.	0.1026	0.0145	150	10	1.8	20°
3.	0.1026	—	150	10	1.8	40°
4.	0.0205	—	150	none	0.3	20°
5.	0.0205	—	150	"	0.8	20°
6.	0.0205	—	150	"	1.3	20°
7.	0.0513	0.0029	145	5	0.9	20°
8.	0.0513	0.0019	145	5	0.9	40°
9.	0.0513	0.0010	145	5	0.9	60°
10.	0.0513	—	145	5	0.9	80°
11.	0.0513	—	145	5	0.9	80°
12.	0.0513	—	145	none	0.9	80°

1, 3, 5, and 6 were very spongy. In 4, 10, and 11 no deposition of metal took place; 12 was spongy and was covered with a white coating of zinc hydrate. At 80° no

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxix., No. 136.

metal was deposited in the presence of free acid, provided the current was not too strong. The ratio of decrease with rise of temperature was:—20—40° 10 grms., 40—60° 9 grms., 60—80° no deposit. The distance between the poles was 2·85 c.m. Area of electrodes (3·8 c.m. × 3·16 c.m.) × 2. Duration of experiment one hour.

III. Influence of Pole Separation upon the Precipitation of Zinc.

	Zinc taken. Grm.	Zinc deposited. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per minute. C.c.	Time. Hours.	Distance between poles. C.m.
1.	0·0102	0·0046	10	700	1·9	3	1·58
2.	0·0102	0·0023	10	700	1·9	3	3·16
3.	0·0102	0·0015	10	700	1·9	3	6·33
4.	0·0102	0·0003	10	700	1·9	3	12·66

Area of electrodes (3·8 c.m. × 3·48 c.m.) × 2. The deposit was firm and compact. Compared with the results obtained with copper and cadmium, the result in 4 is too low.

Lead (Determined Electrolytically).

On account of tendency of lead and manganese to separate in the form of peroxide at the positive pole, it was deemed advisable to make a series of experiments on the metals themselves before attempting to effect their separation. The results were as follows:—

	Lead taken. Grm.	Lead found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per minute. C.c.	Time. Hours.	Difference from theory.
1.	0·1153	—	5	100	1	16	—
2.	0·1153	—	20	100	1·2	48	—
3.	0·1153	—	5	100	2·8	3	—
4.	0·1153	—	20	100	2·8	16	—

Fifty c.c. of a lead formate solution were used in each of the above experiments. In all of them the lead was deposited in a spongy state at the cathode with more or less peroxide on the positive pole.

As the moist metal deposited on the cathode rapidly oxidises, even when adherent and compact, the results obtained are invariably too high, and in practice it is customary to estimate lead as peroxide on the anode, securing its deposition in that form by the addition of nitric acid to the solution. The results obtained with free formic acid, as given above, were not such as to justify attempting its separation from either copper, cadmium, or zinc.

Manganese (Determined Electrolytically).

	Manganese taken. Grm.	Manganese found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per minute. C.c.	Time. Hrs.	Difference from theory. Percentage.
1.	0·0554	0·0552	5	100	2·2	17	—0·36
2.	0·0554	0·0556	5	100	2·7	18	+0·36
3.	0·1108	0·1101	20	100	2·8	24	—0·63
4.	0·0554	—	30	100	1·6	16	—

The platinum dish was made the anode, the wire spiral serving as the negative pole. With small quantities of free acid, 1 and 2, considerable peroxide of manganese separated on both poles; with larger quantities (3, 4) only very slight traces were found on the cathode. The deposition in 4 was not complete. The peroxide formed a black lustrous coating on the dish, adherent while moist, but scaling off upon being heated.

The manganese which separated on the cathode was removed by means of a small piece of filter paper, which was ignited and the ash added to the contents of the dish, which was then raised to an intense heat in order to convert the peroxide of manganese into Mn₂O₃, in which form it was finally weighed. Traces of Mn were found in solution 3.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 17th, 1892.

Sir HENRY ROSCOE, M.P., F.R.S., Vice-President, in the Chair.

ON taking the Chair, Sir HENRY ROSCOE congratulated the Fellows on the very great improvement effected in the Society's rooms, especially in the meeting room, during the recess.

The Treasurer, Professor THORPE, agreed with the Chairman in thinking that the fellows present had good reason to congratulate themselves on the changed conditions under which they met. The meeting room had undergone, as they saw, what was practically complete reconstruction, the position of the table and of the seats having been altered, with the result that not only had a very considerable air-space been gained, which would tend to the better ventilation of the room, but also additional accommodation, both in actual seating space and in the means of entrance and exit, had been secured. Provision had been made for a larger supply of fresh air and for the removal of that which passed into the rooms. Moreover, it would be noticed that the electric light had been substituted for gas as an illuminant throughout the building; this, it was hoped, would promote the comfort of Fellows attending the meetings, not only in its effect on the nature of the air within the rooms, on the cleanliness of the apartments, and on the preservation of their decorative character, but also by affording greater facilities for the exhibition of specimens, diagrams, and lantern projections. It would be understood that the structural and other alterations required by these changes necessarily occupied a considerable time, and although every effort had been made to complete the changes within the recess, it had been considered desirable to postpone the date of the opening meeting to a week or so later than the usual time, in order to secure everything being in proper working order when the Society met. The structural alterations had been planned and their execution superintended by Mr. Martin L. Saunders, to whom the thanks of the Society were due for the care and assiduity with which he had discharged the duty he undertook. These alterations had been made by Messrs. Colls and Son, who had also carried out the re-decoration of the whole of the apartments to the entire satisfaction of the Committee. The installation of the electric lighting was planned by Professor Ayrton, to whom the Society was under a very special obligation for the great amount of time, thought, and energy he had expended on the work. The business of wiring the building and of affixing the fittings was entrusted to Messrs. Spagnoletti and Crookes, with the result that all present were able to enjoy. The fittings, that is, brackets and pendants, were supplied by Messrs. Faraday and Sons, and do credit to the reputation of that firm for artistic work. Experience could alone show how these various alterations would work in practice, but enough had been seen already to indicate that they were undoubtedly great improvements, and would conduce to the health and comfort of the Fellows.

On the motion of the Chairman, seconded by the Treasurer, it was resolved: That the best thanks of the Fellows be tendered to Mr. Martin L. Saunders and Professor Ayrton for their valuable services.

Certificates were read for the first time in favour of Messrs. Robert Samuel Adcock, Rio Tinto Mines, Huelva, Spain; William Smellie Anderson, Marine Station, Granton; David Avery, Queen's College, Melbourne University, Australia; Arthur John Bensusan, 13, Lansdown Road, Kensington Park, W.; and Darling Point, Sydney; Horace Vincent Butfield, 16, Thistlewaite

Road, Clapton, N.E.; Frederick Walter Carlton, Marlow House, Swindon; Ernest Victor Clark, 5, Tisbury Road, West Brighton; Arthur James Cooper, The Schoolhouse, Bromyard, Herefordshire; Andrew William Craig, 77, Peel Street, North Melbourne; Joseph R. Denison, 1, Park View Terrace, Manningham, Bradford; Thomas Duxbury, Richmond Terrace, Darwen; Martin Onslow Forster, 32, Binfield Road, Clapham Road, S.W.; William French, 74, Walmersley Road, Bury, Lancashire; Walter Goodall, Alma House, Pudsey, near Leeds; John Goodfellow, F.R.M.S., 2, Rutland Terrace, High Road, Leyton, Essex; Thomas Gray, 16, Craigmere Terrace, Dowanhill, Glasgow; William Thomas Gronow, Port Pirie Smelting Works, Port Pirie, South Australia; Walter S. Haines, Chicago, U.S.A.; James G. Hardy, 1, Keir Terrace, Pollokshields, Glasgow; Samuel C. Hooker, Philadelphia, U.S.A.; John Horsfall, 88, Scar Terrace, Bacup, Lancashire; Edgar Edward C. Horwill, 104, Ferndale Road, Clapham, S.W.; W. H. Ince, Ph.D., 12, Cowley Street, Dean's Yard, Westminster; John F. V. Isaac, 8, Montserrat Road, Putney, S.W.; John Jackson, Rhymney; Samuel Jackson, Nether Thong, Huddersfield; William George Johnson, 4, Hilgrove Road, Finchley Road, Hampstead, N.W.; K. K. Kacker, Delhi, India; Thomas Torrens Knowles, School House, Lancaster; G. Krause, Cöthen (Anhalt, Germany); Thornton Charles Lamb, Polygon, Ardwick, Manchester; William Howard Lloyd, 5, Belmont Villas, New Walk, Leicester; Arnold G. Maddox, 15, Fleetwood Street, Clissold Park, N.; Colin Francis Moorwood, 260, Barnsley Road, Sheffield; J. B. Nickolls, 8, College Terrace, Grange, Guernsey; Hugh Ramage, Royal College of Science, Dublin; James Wylie Rodger, 76, Anerley Park, S.E.; Norman Scott Rudolf, Sewan Sarun, Bengal, India; Satyaprasad Sarbadhicary, 53, Wellington Street, Calcutta; Augustus Schloesser, Ph.D., M.Sc., 7, Victoria Crescent, Busby, Near Glasgow; William James Sell, 1, Bene't Place, Cambridge; George Arthur Shaw, 112, Bramhall Lane, Stockport; Reginald des Foyes Shepherd, 6, Coleman Street, Hull; Charles Spackman, Sibley, Loughborough; Ernst Speidal, B.S., 17, Quincey Street, Chicago, Illinois; A. H. Turton, Ashley, Carlisle Road, Edgbaston; Frederick William Westaway, 1, Aytoun Road, Stockwell, S.W.; John Lowe Whiteside, 51, Canon Street, Bolton; Frederick Henry Wigham, 25, Pinderfield Road, Wakefield; William Williams, Smithfield Street, Dolgelly, N. Wales; N. T. M. Wilsmore, Altona, Orrony Road, Elsternwick, Melbourne.

The CHAIRMAN announced that the following Address had been forwarded to the sister society in Berlin;—

Address to the Deutsche Chemische Gesellschaft.

The Chemical Society of London desires to offer its warmest congratulations to the Deutsche chemische Gesellschaft on the occasion of the celebration of its Twenty-fifth Anniversary; while, at the same time, it joins with the Sister Society in deploring most deeply the recent irreparable loss of one who was long so intimately associated with both bodies,—who exercised so important an influence on their development, and who took so large a share in the guidance of the affairs, first of the one and then of the other.

The Chemical Society of London is proud to think that it may properly regard the German Society as its direct lineal descendant through Hofmann. No offspring could possibly have done greater credit to its parent; indeed, the rapidity of growth and youthful vigour of the offshoot is beyond all precedent. A true mirror of the progress of chemical science, the stately series of volumes issued by the Society during the first quarter-century of its existence, will ever serve as the priceless historical record of the marvellous advance of chemistry during the period; and that advance would appear to be in no small degree due to the incitement afforded to experimental inquiry by the regular and frequent issue of the now far-famed *Berichte*.

But probably it will in the future come to be regarded as the greatest service of the Deutsche chemische Gesellschaft that it has done so much to render possible the ultimate denationalisation of chemical science. Chemists of all nations record their results in the pages of its publication, which has become a meeting ground where international jealousies disappear and the spirit of utmost toleration prevails. No one more clearly recognised the greatness of such a service than Hofmann. In 1863, when President of the Chemical Society of London, speaking at the Twenty-second Anniversary Meeting of the delivery of lectures to the Society by distinguished foreign chemists, he said: "The Chemical Society has loudly proclaimed the cosmopolitan character of science, and that henceforth it will look upon the several nations engaged in scientific pursuits as upon so many federal members of a great Republic united by the love of science, and pledged by contributions to a common treasury, as it were, to uphold its cause and to raise its dignity." The cosmopolitan influence of the great moving spirit of its councils during the first twenty-five years of the existence of the Deutsche chemische Gesellschaft will ever be regarded as a priceless service rendered to chemical science by Hofmann.

The following resolution was passed at the meeting of the Council in the afternoon:—

"The Council learns with deep regret that, through the death of Dr. Longstaff, on the 23rd September last, the Society has lost its senior Fellow and one of its founders. The deep interest which Dr. Longstaff took in the Society, and in the promotion of the interests of chemical science, having been evinced by the munificent gift which secured the establishment of the Research Fund, his name will ever remain associated with the history of the Society, and will be retained fresh in the memory of the Fellows through the triennial award, to those who have distinguished themselves in chemical research, of the Medal bearing his name."

The following papers were read:—

63. "*Fluosulphonic Acid.*" By T. E. THORPE, F.R.S., and WALTER KIRMAN.

The authors have prepared this compound by distilling a slight excess of hydrogen fluoride into a weighed platinum flask containing a known amount of sulphuric anhydride, both the condensing tube and the receiver being surrounded with a mixture of ice and calcium chloride; the excess of hydrogen fluoride was subsequently removed by passing a current of dry carbon dioxide through the liquid product at a temperature between 25° and 35°. The interaction is attended with the development of much heat.

Fluosulphonic acid, SO_3HF , is a thin colourless liquid boiling with slight decomposition (apparently into SO_2F_2 and SO_4H_2) at 162.6°, which, it is noteworthy, is a higher temperature than that at which chlorosulphonic acid boils (155.3°). It has but little action on the dry skin, feeling greasy to the touch, and being without the intense blistering action of hydrogen fluoride.

DISCUSSION.

Professor RAMSAY expressed the opinion that the name fluosulphonic acid was preferable to fluosulphonic acid.

Mr. PAGE and also Sir HENRY ROSCOE asked whether the isolation of fluorine had been confirmed by any independent observer since the announcement of Moissan's discovery.

Dr. ARMSTRONG said the fact that fluosulphonic acid had a higher boiling point than chlorosulphonic was of special interest, as in the case of corresponding "atomic" compounds the fluorine compound, as a rule, had a lower boiling point than the chlorine compound; he thought that on the whole the evidence favoured the view that chlorosulphonic acid was a so-called molecular compound, and, perhaps, an explanation was to be found in this

direction. He suggested also that probably the fluor- and chlor-acids would be found to yield the pyrofluoride and pyrochloride, and not the sulphuryl compounds on distillation.

Professor THORPE, in reply, said that he had no special views with regard to the use of the syllable fluor instead of fluo. He had spent considerable time in attempting to repeat Moissan's work, without obtaining definite results; but possibly he had not had the good fortune to hit on the precise experimental conditions requisite for success. He had, however, given Moissan a long account of his trials without obtaining any specific information from him in reply.

64. "Note on the Interaction of Iodine and Potassium Chlorate." By T. E. THORPE, F.R.S., and GEORGE H. PERRY.

The interaction is usually represented by the equation $3\text{KClO}_3 + \text{I}_2 = \text{KClO}_4 + \text{KCl} + \text{KIO}_3 + \text{ICl} + \text{O}_2$; the authors find, however, that it primarily and in the main involves a simple interchange of iodine and chlorine:—



When care is taken in heating the mixture, it is possible to convert practically the whole of the iodine present into potassium iodate, the equivalent amount of gaseous chlorine being liberated.

65. "The Magnetic Rotation of Sulphuric and Nitric Acids, and of their Aqueous Solutions; also of Solutions of Sodium Sulphate and Lithium Nitrate." By W. H. PERKIN, Ph.D. F.R.S.

The author has previously shown that, although the molecular rotations of the fatty acids and their ammonium salts are not appreciably influenced by the presence of water, yet that of sulphuric acid is to a considerable extent, the rotation rapidly falling for small dilutions, but diminishing as the amount of water is increased; in these experiments the examination was only extended to a mixture corresponding to $\text{H}_2\text{SO}_4 + 3\text{OH}_2$. Nitric acid was also found to behave in a similar manner.

On account of remarks by Professor Ostwald on these results, and the interest which is taken in the subject of solutions, a more extended series of observations has been undertaken. The results are given in the paper in a tabular form, and are also represented graphically. In the case of sulphuric acid and sodium sulphate it is shown that there is no apparent connection between the value for the rotation and extent to which dissociation is supposed to take place, down to solutions containing about 9 per cent of acid or 12 per cent of sodium sulphate. The same conclusion was come to from the examination of solutions of these substances at temperatures of about 90° , when the rotation increased instead of diminishing, as it should have done, according to the dissociation hypothesis. The results, however, are not inconsistent with the assumption that combination takes place with the formation of $(\text{HO})_4\text{SO}$.

The results obtained with nitric acid give a different kind of curve to that afforded by sulphuric acid, viz., one consisting of a practically straight line down to solutions containing about 33 per cent of HNO_3 , after which it appears to curve somewhat downwards; and, although it does not deviate so much as sulphuric acid from that representing the dissociation, yet it does not correspond at all closely with it. It is considered that these results may indicate the formation of a compound resulting from the union of the acid with water, e.g., $(\text{HO})_3\text{NO}$.

Lithium nitrate resembles nitric acid in its behaviour. The rotations of the haloid hydrides in aqueous solution are also referred to, showing that as those of the concentrated solutions at first change very rapidly with small dilutions, but more slowly with large dilutions, at last becoming nearly stationary, they are not in agreement with their dissociation, which increases with dilution.

66. "Note on the Refractive Indices and Magnetic Rotations of Sulphuric Acid Solutions." By S. U. PICKERING.

The values for the refractive indices of these solutions obtained by van der Willigen when plotted out and examined by a flexible lath, show the existence of a well-marked "break" as well as a maximum at 84.5 per cent (the monohydrate), another "break" at 57.7 per cent (the tetrahydrate), and another at 24—30 per cent. The first two of these agree with the breaks shown by the magnetic rotations, and all three of them agree with breaks found in the examination of other properties. The experimental points available were not sufficiently numerous to indicate more than the most prominent "breaks," and it was found that the densities when treated so as to lead to the indications of the most prominent "breaks" only, indicated these same three. For this purpose the molecular volumes were calculated from the densities of solutions of the same strength as those used by Dr. Perkin, and when plotted out they showed "breaks" at 83.5, 60, and about 30 per cent. When the same number of values, but for solutions of different strengths, were taken, the same "breaks" were still indicated.

DISCUSSION.

Professor RAMSAY drew attention to a work by van der Waals, on the continuity of the liquid and gaseous states, the fundamental equation underlying all the calculations in which is—

$$p = \frac{RT}{(v-b)} - \frac{a}{v^2}.$$

This expression, graphically interpreted, gives a curve of double flexure, with very abrupt changes of curvatures, provided numbers be appropriately chosen. (The curve was drawn on the blackboard.) He entirely dissented from Mr. Pickering's conclusions as regards "breaks," and denied the existence of anything but continuous transitions from one state to another; and he maintained that it was no more sensible to attempt to detect "breaks" with a bent lath than to assume that all curves were parabolas or circles.

Dr. WALKER drew attention to the circumstance that, in calculating the amount of electrolytic dissociation from the electrical conductivity of mixtures of sulphuric acid and water, Dr. Perkin had neglected to take account of one of the factors which determine the conductivity, namely the speed of the ions, which is intimately connected with the viscosity of the solutions. His "dissociation" curves, therefore, did not represent at all the actual degree of dissociation in the strong solutions studied by him, for in them the viscosity is comparatively great. The same objection applied to the temperature experiments. The great increase of conductivity caused by elevation of temperature is due almost exclusively to the increased speed of the ions, and not to any change in the dissociation. In his opinion, therefore, the conclusions drawn by Dr. Perkin as to the want of concordance between his results and the theory of electrolytic dissociation were from this cause invalid.

Mr. PICKERING, in reply to Professor Ramsay, said that, as he had long ago pointed out, there were, of course, many classes of curves which were not amenable to treatment with a flexible lath; the fact that Prof. Ramsay was able to instance one of these neither proved nor disproved anything.

67. "The Hydrate Theory of Solutions. Some Compounds of the Alkylamines with Water." By S. U. PICKERING.

In making a series of determinations of the freezing-points of solutions of these amines, it was found that most of them formed one or more definite crystalline hydrates. Sixteen amines were examined, of which two were entirely and two very sparingly soluble, and twenty-four hydrates in all were isolated. Hydrates with the same number of water molecules occur in many different cases, but no connection could be traced between the degree of hydration and the nature of the amine. Indications of hydrates were also obtained by "breaks" in

the curves representing the freezing-points, and in every instance but one a hydrate of the composition thus indicated in the case of one amine was actually isolated in the crystalline condition in the case of some other amine. The lowest hydrate isolated (in four cases) contained $\frac{1}{2}\text{H}_2\text{O}$, and the highest $11\text{H}_2\text{O}$. The freezing-points of the hydrates ranged from $+5^\circ$ to -71° . In the case of the amines themselves, as well as of such hydrates as contain the same number of water molecules, the freezing points seem to fall as the number of carbon atoms present in the alkyl radicle increase, and to rise as the number of radicles in the amine increases. The following is a list of analysed hydrates isolated as crystals:—

$\text{EtNH}_2, 5\text{H}_2\text{O}$,	$\text{EtNH}_2, 5\frac{1}{2}\text{H}_2\text{O}$,
$\text{PrNH}_2, 5\text{H}_2\text{O}$,	$\text{BaNH}_2(\text{iso-}), 7\text{H}_2\text{O}$,
$\text{Et}_2\text{NH}, 5\text{H}_2\text{O}$,	$\text{Me}_2\text{NH}, 7\text{H}_2\text{O}$,
$\text{Pr}_2\text{NH}, 5\text{H}_2\text{O}$,	$\text{PrNH}_2(\text{iso-}), 8\text{H}_2\text{O}$,
$\text{Me}_2\text{NH}, \text{H}_2\text{O}$,	$\text{PrNH}_2, 8\text{H}_2\text{O}$,
$\text{Et}_3\text{N}, 2\text{H}_2\text{O}$,	$\text{Et}_2\text{NH}, 8\text{H}_2\text{O}$,
$\text{Me}_3\text{N}, 3\text{H}_2\text{O}$,	$\text{Me}_3\text{N}, 11\text{H}_2\text{O}$.

DISCUSSION.

Professor THORPE, after referring to the fact that the late Professor Guthrie had investigated the relationship of certain of the alkylamines to water as far back as 1884 (*Phil. Mag., Proc. Phys. Soc.*, 1884, 169), said that among other things Guthrie had pointed out that while a mixture of triethylamine and water containing from 15 to 50 per cent of the alkylamine was clear and transparent at ordinary temperature, on warming it became suddenly turbid owing, apparently, to the triethylamine being thrown out of solution. On cooling the liquid it again became clear, but could again be rendered turbid on warming. The temperature at which this change occurs is remarkably constant, viz., about 18.4° . In this behaviour a solution of triethylamine in water resembles an aqueous solution of ammonia. It occurred to the speaker to try whether the effect of pressure on the solution would be to increase the apparent solubility of the alkylamine in water by observing whether the turbidity would disappear under pressure, the temperature being maintained above 18.4° . Experiments showed that this was the case. By enclosing a quantity of the solution in a Cailletet tube, to which pressure could be applied in the ordinary way by the Ducretet pump, it was found that on rendering the liquid turbid by surrounding the tube with tepid water, the turbidity almost instantly disappeared when the pressure was increased a few atmospheres, and as quickly reappeared on releasing the pressure. Professor THORPE proceeded to demonstrate this phenomenon with the aid of the electric light by throwing an image of the tube on the screen. On gently warming the tube the solution became so turbid as to practically stop the passage of the light. On applying pressure, the solution was seen to clarify, but on releasing the pressure it again became milky, and, in fact, nearly opaque.

68. "The Atomic Weight of Boron." By EMILY ASTON, B.Sc. (Lond.), and WILLIAM RAMSAY, Ph.D., F.R.S.

An account is given of the re-determination of the atomic weight of boron by two methods: by the determination of the water of crystallisation in borax, and by the conversion of anhydrous sodium borate into sodium chloride by distillation of the borax with chlorhydric acid and methyl alcohol, and weighing the resulting sodium chloride.

The aggregate of seven experiments in which 42 grms. of borax were deprived of water gave as atomic weight 10.921 , with a probable error of 0.01 .

Two series of experiments were made in which borax was converted into sodium chloride. The first series, in which over 20 grms. were employed, gave as atomic weight 10.942 ; the second series, in which more than 23 grms. were converted, gave as atomic weight 10.966 . The result of the second series is regarded as more probably correct.

The authors discuss the discrepancy between their results and Abrahall's (*Chem. Soc. Trans.*, 1892, 650) and give reasons why they regard the value deduced by this observer (10.825) as too low; they think that his boron bromide may have been contaminated with hydrogen bromide present as $\text{BBr}_3 \cdot \text{HBr}$.

69. "Methoxyamido-1:3-Dimethylbenzene and Some of its Derivatives." By W. R. HODGKINSON and LEONHARD LIMPACH.

Having devised a method of separating 1:2:4-metaxylidine from paraxylidine, &c., with which it is mixed in commercial xylidine, the authors have had the opportunity of preparing 1:2:4-metaxylenol in large quantity. An almost theoretical yield of this phenol was obtained by diazotising a solution containing only 5 per cent of the xylidine sulphate and then steam distilling; the product did not solidify even at -20° , but a considerable quantity was caused to crystallise by adding solid, obtained by cooling a small portion by means of carbon dioxide and ether. The presence of a trace of water was found to prevent crystallisation. On nitration, metaxylenol yields almost the theoretical amount of a nitroxylenol, in which the NO_2 group is contiguous to the hydroxyl. The authors have prepared the corresponding amido- and hydroxy-xylenols and their methylated derivatives (dimethylanisols); they also describe a quinaldine derivative, formed by condensation from the methoxy-amidoxylene and ethylic acetoacetate.

Extra Meeting, December 13th.

An Extra Meeting of the Society will be held on Tuesday, December 13th, at 8 p.m., the Anniversary of the death of Stas. A paper, specially prepared for the occasion by Professor J. W. MALLET, F.R.S., entitled "Jean Servais Stas, and the Measurement of the Relative Masses of the Atoms of the Chemical Elements," will be read and discussed.

PHYSICAL SOCIETY.

Ordinary Meeting, November 25th, 1892.

Prof. S. P. THOMPSON, D.Sc., F.R.S., Vice-President, in the Chair.

MESSRS. T. J. Fry, A. G. Bessemer, junr., and E. T. Fournier d'Abbe were elected Members.

The following communication was made:—

"Experiments in Electric and Magnetic Fields: Constant and Varying." By MESSRS. RIMINGTON and WYTHE SMITH.

In the first set of experiments shown, exhausted electroless tubes and bulbs were rotated rapidly in a constant electric field between two parallel charged discs. Double fan-shaped images were produced by the tubes, due to the displacement currents which pass to equalise the potentials at the ends of the tubes. These fans were not symmetrical with respect to the lines of electric force, but were displaced in the direction of rotation. In explanation of this phenomenon it was pointed out that as a tube rotated, the potential difference between its ends increased until this difference was sufficient to break down the dielectric in the tube. The discharges would therefore pass at the ends of the intervals during which the difference of potential was rising, and consequently the images would be displaced from the symmetrical position in the direction of rotation. The number of discharges produced during one revolution was found to depend on the strength of the electric field, but not on the speed of rotation, and that end of the tube which was approaching the negatively charged plate appeared brightest. These experiments were referred to as examples of the direct conversion of mechanical energy into light. Instead of rotating tubes in a constant electric field the tubes were next kept stationary, and a varying electric field produced

by connecting the plates with an influence machine allowed to spark; under these conditions the tubes and bulbs were seen to glow. Using large suspended plates charged by an induction coil, long tubes were caused to glow brightly even at considerable distances away from the plates. The glow could be apparently wiped out by passing the hand along the tube.

Another series of experiments were performed in varying magnetic fields. With a view to showing Hertzian phenomena to large audiences the authors tried Geissler tubes to replace the spark gap in resonators with great success. When large Leyden jar circuits were used, the effects were very brilliant. Another form of resonator consisted of a bent wire terminating in two plates, between which an exhausted tube was placed. This tube became luminous when the resonator was placed in the vicinity of a fairly large Hertz oscillator.

Other experiments similar to those shown before the Society at Cambridge by Prof. J. Thomson, on discharges in exhausted bulbs were then made, the bulbs being placed with a coil of wire of four turns, forming the connection between the outer coatings of two small jars, whilst sparks passed between knobs connected with the inner coatings. The bulbs glowed brightly at each discharge, rings of light being seen near their inner surfaces. On putting a ring tube outside the coil this was also seen to glow. The most brilliant part of the glow always occurred in close proximity to the wire coil.

A secondary coil, wound by the side of the above-mentioned primary, could be short-circuited at will; this had the effect of decreasing or extinguishing the luminosity in the bulb or tube. Bright sparks passed between the secondary terminals when held a short distance apart, but the shock experienced by touching the ends was not serious.

The above arrangement, with the addition of two Geissler tubes placed in series between the outer coatings of the jars, was used to illustrate the fact that closing the secondary diminishes the impedance of the primary circuit of a transformer.

Experiments on condensers made of tin-foil on glass were shown. In one of them, parts of the coatings in the form of letters had been removed, and the spaces became luminous when the condenser was connected with an induction coil. In another experiment a glass plate was moved to and from a condenser, and a musical note could be heard whose pitch increased as the distance between the glass plates diminished. The note was said to be the octave of an open organ pipe whose length was equal to the distance between the plates.

Mr. SWINBURNE thought some of the effects shown were not Hertzian, but merely cases of ordinary mutual induction. He enquired whether the vacuum tubes would still glow if the Leyden jars were removed from the so-called resonating circuits. He was also of opinion that in the magnetic experiments the surfaces of the bulb, and not the enclosed gases, took the charges.

Mr. WATSON asked if the authors had tried screening off the long waves by a wet cloth. If the effects still existed this would prove that they were Hertzian.

Mr. BLAKESLEY wished to know if the images of the rotating tubes were at equal angular distances.

Mr. SMITH pointed out that these distances were not equal, but corresponded to equal changes of potential.

Prof. AYTON remarked that the only cases where the materials of the bulbs, tubes, &c., did not influence the results were those in which discharges were produced by varying magnetic fields.

Mr. E. T. CARTER thought an induction coil a more efficient machine for producing the glow in tubes than the alternator, &c., used by Mr. Tesla.

Mr. TROTTER asked if the authors had observed whether the glow produced by passing a discharge through a wire wound in a long pitch spiral round a tube formed an open or a closed circuit of light.

Prof. S. P. THOMPSON said he first noticed that sparks

passed between pieces of metal in the vicinity of an induction coil sparking into a condenser in 1876, when he was showing some experiments on telegraphic apparatus before the Society, but unfortunately he did not pursue the subject. Long before Mr. Tesla's investigations Dr. Bottomley had shown that exhausted tubes could be caused to glow, but it was not until Tesla produced such phenomena on a large scale that people recognised how much light could be got in that way.

Mr. RIMINGTON, in replying to a question by Professor Thompson, said the notes heard when the glass plate approached the condenser were of very high pitch. The explanation, why in the experiments performed in varying magnetic fields the bright parts of the luminous discharges were near the wire, appeared to be that the E.M.F. was greatest in these places. Although he had not tried the experiment suggested by Mr. Swinburne of taking off the Leyden jar, he felt sure that doing so would stop the glow.

NOTICES OF BOOKS.

Lightning Conductors and Lightning Guards. A Treatise on the Protection of Buildings, of Telegraph Instruments and Submarine Cables, and of Electric Installations generally, from Damage by Atmospheric Disturbances. By OLIVER J. LODGE, D.Sc., F.R.S., LL.D., M.I.E.E., Professor of Physics in University College, Liverpool. London: Whittaker and Co., and G. Bell and Son.

In this work it is very fully shown that the possible mischief of a lightning flash is resolvable into two elements: (1) its disruptive or explosive violence; and (2) its heat. The former effect is most to be dreaded when the flash is well conducted except at a few places, and the latter when it encounters great resistance. In Britain a thunderstorm is generally accompanied with a third kind of mischief more to be dreaded than the ignition of houses or the destruction of a few men or cattle: the weather is too generally upset for at least a week—a loss which in the midst of our brief summer is tantamount to an impaired harvest. But whether the wave of cold is the cause or the effect of the electric action, it is an evil for which our electricians see at present no remedy. Dr. Lodge points out that leading the charge to earth does not always get rid of it, as it may rise again until the energy is consumed.

The present ideas—perhaps we might better say those of a time but recently past—concerning electric conductors are shown to be in many respects defective, and as sometimes leading to undesirable results. Lightning has strange vagaries against which it is not always possible to provide. Everything which projects upwards should be spiked, but very high rods do not appear desirable. For the conducting rods, iron, though less perfectly conductive than copper, is preferred, chiefly because it is much less likely to be stolen. Says Dr. Lodge:—"Let the lightning come to you; do not go to meet it. Protect all your ridges and pinnacles, not merely the highest, and you will be safer than if you built yourself a factory chimney to support your conductor upon. At present the immediate neighbourhood of a factory chimney or a steeple is not a safeguard, but a source of mild danger even when itself thoroughly protected. If it have no conductor, it is no doubt still more dangerous."

Dr. Lodge recommends that metal gutters, balconies, &c., should be connected at both ends. Leaden water-pipes and gas-piping inside a house should not be connected.

The system recommended by Clerk-Maxwell is totally different. He seeks to enclose a house, or still more a magazine in a stout wire cage.

It is a remarkable and unpleasant fact that the Hôtel de Ville at Brussels, the most perfectly and elaborately

protected building in the world, the masterpiece of M. Melsens, has been struck and set on fire.

Contrary to received ideas, lightning has been known to penetrate into a railway tunnel, into coal mines, into cavities surrounded by high buildings with leaden roofs, iron water-pipes, and iron portcullis, to get at a steel gas bracket. The insulation, or attempted insulation, of conductors is condemned on the faith of actual observation.

Dr. Lodge has, by the publication of this work, done good service to all who require lightning conductors or have to fit up these protectors.

Explosives and their Powers. Translated and Condensed from the French of M. BERTHELOT by C. NAPIER HAKE, F.I.C., Inspector of Explosives to the Government of Victoria; and WILLIAM MACNAB, F.I.C. With a Preface by Lieut.-Colonel J. P. CUNDILL, R.A., H.M. Inspector of Explosives. With Illustrations. London: John Murray, 1892.

THIS elaborate work is not, like, *e.g.*, that of Eissler, a practical treatise on the manufacture, the analysis, and the uses of the various explosives now known. Its central idea is the application to the study of explosives of thermo-chemistry, well known as the speciality of M. Berthelot. Setting out from this basis, the author expounds the general properties of explosives, those features upon which their efficacy depends.

The author considers that explosive substances are characterised by the sudden development of a considerable expansive force, by which means they effect enormous mechanical work. Such work, however, it must be admitted, is mainly of a destructive character. The "unspeakable advantage" due to the replacement of the old war appliances has its fearful set-off in the facilities which the so-called high explosives now offer to the criminal and the conspirator.

In the action of explosives two orders of effects have to be distinguished: the one due to pressure, and the other to the work developed, or, practically speaking, to the heat liberated. Here attention is called to the fact that the products developed at the moment of the explosion are not necessarily the same as those found after cooling. The heat liberated is calculated from our examination of the products of the reaction, though a part of this heat is transformed into work. The pressure exerted is calculated from the volume of gas liberated. The duration of the transformation is an important characteristic of an explosive. It is found that nitro-glycerin and gun-cotton explode in a quite different manner, according to the manner of their ignition. They may burn away quietly or they may exert violent shattering effects. The latter result occurs chiefly when mercury fulminate is used as a primer.

It is, of course, impossible to enter into the details of this work; but there is one statement which we can notice only with profound regret. M. Berthelot writes:—"The explosion which happened in 1871 in the Stowmarket factory, and in which twenty-four persons perished, was attributed, rightly or wrongly, to imperfect supervision." The verdict of the jury, founded on the unanimous evidence of the scientific experts called, was that a portion of the gun-cotton had been tampered with after the manufacturing process was completed. This conclusion was reached alike by the chemists representing the Home Office, the War Department, and the Gun-cotton Company. Nor, as we well remember, could the facts admit of any other possible interpretation.

If we set this one unfortunate passage aside, the work will be of the highest value to manufacturers of explosives.

On Certain Crystalline Sodium Titanates.—H. CORMIMBOEUF.—Sodium sesquitanate has the composition $3\text{TiO}_3 \cdot 2\text{NaO}$; the sodium bititanate is $2\text{TiO}_2\text{NaO}$; the trititanate is $3\text{TiO}_2\text{NaO}$.—*Comp. Rend.*, cxv., No. 20.

CORRESPONDENCE.

THE CHARTER OF THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—It is pretty well known amongst the Members of the Institute of Chemistry, that for some considerable time past the Council has been engaged in considering a scheme for the re-arrangement of the system of examinations at present adopted in reference to admission to the Institute, and that unexpected difficulties have arisen through the nature of the wording of the Charter. As originally drafted, a principal feature in the proposed new system was substantially the carrying into effect of the views of the writer put before the Institute Conference, held in May, 1891, as regards the necessity for further extending the examinational system. At present, this only deals with what may be conveniently termed the *preliminary scientific* training of the candidate, and does not embrace any adequate testing of the nature and extent of the *professional training* acquired subsequently to duly laying the foundations of his scientific education.

Obviously, to render the possession of the Fellowship of the Institute of Chemistry a guarantee of competency "to practise in analytical chemistry, and to advise in technological chemistry" (to quote from the Charter), the tests of competency hitherto applied require considerable extension; if the Institute is to issue a certificate implying that the holder thereof has been found to possess proper qualifications so to practise and advise, it must thoroughly sift and test the attainments of each candidate in at least some one branch of analytical chemistry as employed in professional practice, or of technological chemistry: *i.e.*, the proficiency of each candidate in the branch selected by him must be ascertained and duly authenticated; so that he would take his Fellowship in, for example, the branch of metallurgical chemistry, or in that of the manufacture of dyeing materials and their employment in dyeing textile fabrics, or in that of food and drug analysis, &c.

It is evident from the wording of the Petition presented to H.M., praying that a charter should be granted, that the object sought was the empowering of the Institute to grant *certificates of professional competency* to such persons as should be found duly qualified to hold them. This clearly results from the above quotation and the following ones (the italics are the writer's). "The Society aims at the elevation of the profession of consulting and analytical chemistry, and the promotion of the efficiency and usefulness of persons practising the same, by compelling the observance of strict rules of membership, and by setting up a *high standard of scientific and practical proficiency*." "It would greatly promote the objects for which the said Institute has been instituted, and would also be for the public benefit, if the members thereof were incorporated by Royal Charter with power to afford facilities for the *better education and examination* of persons desirous of qualifying themselves to be *public and technical analysts* and *chemical advisers* in scientific subjects of public importance, and with power to grant such *certificates of competency*."

The present system of examinations certainly tests more or less satisfactorily the candidate's knowledge of general theoretical chemistry and various allied subjects, as well as of the ordinary kinds of laboratory manipulations and processes taught in a college laboratory of the usual type; *i.e.*, it tests his possession of a fairly sound foundation on which the superstructure of professional acquirements may be subsequently raised. This is good as far as it goes, but it falls a long way short of thoroughly carrying out the objects aimed at by the petitioners and by the founders of the original Institute of Chemistry previously incorporated: because the passing of examinations of the kind hitherto conducted affords no adequate guarantee of ability, without further special training, to

practise analytical chemistry as met with professionally (e.g., in the laboratory of a works or of a public analyst), or of competency to advise in technological chemistry or in scientific subjects of public importance; whereas the avowed object of the petitioners was to obtain power to grant certificates which should be such a guarantee, founded on the having given proof of possessing the requisite knowledge and experience.

It is perfectly true that there are very great difficulties indeed in the way of accurately ascertaining the strictly professional qualifications of candidates, apart from their scholastic attainments; i.e., in gauging the extent of their further knowledge of chemistry as applied to arts and manufactures and the wants of the general public, acquired *after* leaving the training college, or having otherwise obtained the requisite preliminary scientific education. But it is equally true that the object set forth by the petitioners in seeking a Charter was substantially to attempt to overcome these difficulties, and ensure that the possession of the Fellowship of the Institute of Chemistry should be of itself an attestation of professional competence,—a result hitherto not attained to any notable extent, wherefore the attempts of the Council to improve matters in this respect.

It might naturally be supposed that when a Royal Charter has been applied for to enable the petitioners to do certain things, and has been duly granted in consequence, the document would be so worded as at least to convey the idea that the powers prayed for have been actually conferred; but as regards the Charter of the Institute of Chemistry this appears not to be the case. To the layman's eye the clauses relating to the admission of Fellows simply exhibit the orthodox want of clearness and precision befitting a legal document when perused by a being of only ordinary intelligence; but to the legal vision they imply much more—no less, indeed, than the absolute prohibition from doing the very thing for which the Charter was most wanted! Such, at least, appears to be the result of "Counsel's opinion" upon the question as to whether an examination can or cannot be imposed on candidates for Fellowship. In short, it seems that the Charter, the object of which was to enable the professional competence of Fellows to be ascertained and certificated, does not permit the Institute to accomplish the *raison d'être* of its existence!

The nett result of this somewhat startling discovery is that in the new scheme recently elaborated by the Council for improving the examinational system, it has been found impracticable to do anything whatever in the way of subjecting to a thorough sifting and testing process the professional qualifications for Fellowship possessed by candidates for that rank; so that in future, as heretofore, the possession of the Fellowship will be in no way a guarantee of sound *professional* training in some particular given direction, but will only imply that a decent sort of *preliminary* scientific education has been obtained.

It becomes, therefore, a matter for serious consideration as to whether steps should not be speedily taken with the object of resigning the present Charter and obtaining instead a new one wherein the powers prayed for are actually given without the possibility of mistake or misconstruction.

In a short time the Annual Meeting of Members will take place, when it might be well that this question should be discussed. As the writer's term of office on the Council will then expire, it will be out of his power to put forward his views in the ensuing year before the then reigning Council; wherefore the present communication.—I am, &c.,

C. R. ALDER WRIGHT.

THE VOLATILE FATTY ACIDS OF BUTTER.

To the Editor of the Chemical News.

SIR,—I must ask you to allow me space in your next issue to reply to Mr. H. Droop Richmond's "Note" in

the CHEMICAL NEWS, vol. lxvi., p. 235, known, in legal phraseology, as constructive libel.

I am obliged to my critic for calling my attention to the error; it is a clerical one, one of transition when calculating the percentage, not an arithmetical one, such as that made by Mr. H. Droop Richmond in his readable English; and, before he becomes an authority on simple arithmetic, it is to be hoped he will study the subject more closely, for by so doing "There is hope, then, that in a few years he may find the same results as other observers."

I refrain for the present from commenting further upon his communication, but I think it would be advisable if Mr. Richmond would unreservedly withdraw his insinuations, as I candidly admit that with this particular sample I cannot go beyond the guarantee of the Aylesbury Dairy Co., from whom I received the butter, and I have every reason to believe it was the best English butter.—I am, &c.,

WILLIAM JOHNSTONE.

13, Fish Street Hill, London.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 20, November 14, 1892.

Combustion-Heat of Camphor.—M. Berthelot.—M. Louguinine found for the different isomeric states of camphor the following combustion-heats:—Dextrorotatory, 1404.2 cal.; levorotatory, 1416.0 cal.; inactive, 1415.4 cal. M. Stohmann, on the contrary, obtained for dextrorotatory camphor 1414.3 cal., and requested M. Berthelot to verify the result. Three determinations were accordingly made by different experimentalists. M. Matignon obtained +1414.2 cal.; M. Tassilly +1413.5 cal.; M. Aladern (mean) +1413.3 cal.

Observations on A. Colson's Paper on the Rotatory Power of the Salts of Diamine.—C. Friedel.—The plane which M. Colson takes as the plane of symmetry is not even a plane of symmetry in inactive tartaric acid, but perpendicular to the only plane of symmetry existing in the molecule constructed with representative tetrahedra.

Researches on the Chemical Constitution of Peptones.—P. Schutzenberger.—(1) The products precipitable by phosphotungstic acid present between the oxygen and the nitrogen a ratio approaching 1.27:1, and between the carbon and the hydrogen a ratio close upon 1:1.9. Under the action of baryta they lose nearly a

fourth of their nitrogen as ammonia ($\frac{1}{3.66}$), a corresponding quantity of carbon dioxide (CO_2 for 2NH_3). The fixed and amidic residue from this treatment with baryta is of the form $\text{p}(\text{C}_n\text{H}_{2n}\text{N}_2\text{O}_4)$, or $\text{C}_m\text{H}_{2m}\text{NO}_2$, n being between 9 and 10 and bordering closely upon 9. (2) Products not precipitable by phosphotungstic acid present between oxygen and nitrogen a ratio near 2:1, and between carbon and hydrogen a proportion near 1:1.7. Under the influence of baryta they lose one-fifth of their total nitrogen in the form of ammonia, and a corresponding quantity of carbonic acid (CO_2 for 2NH_3), as also acetic acid (about 1 mol. for 2 mols. ammonia). The fixed and amidic residue of this treatment is of the form $\text{p}(\text{C}_n\text{H}_{2n}\text{N}_2\text{O}_6)$, or $\text{C}_m\text{H}_{2m}\text{NO}_3$, n comprised between 9 and 10 and very close upon 9. The portion soluble in alcohol gives analogous results, with the difference that there is an excess of hydrogen, the proportion C_nH_{2n} becoming close upon $\text{C}_n\text{H}_{2n}+2$.

Influence of the "Distribution" of Manures in the Soil upon their Utilisation.—H. Schloesing.—The author gives the results of his experiments in the form of tables.

Study on the Pathogenic Power of Beetroot Pulp which has been Ensilaged.—M. Arloing.—The alimentary use of the pulp of beetroot preserved in silos produces various diseases in ruminants, sometimes with a fatal termination. The fatal dose of the juice drained from the pulp varies from 3 to 4 c.c. per kilo. of the living weight of the animal experimented upon. The liquid is most dangerous if the pulp has been kept in a silo for two months. The microbia suspended in the liquor play a less important part in the poisoning cases than the liquid itself. The poison resides in substances of microbian origin dissolved in the liquid. The author divides these substances into diastasic and ptomainic. The latter are convulsing and paralysing, whilst the former exert a more persistent influence of the vaso-motive phenomena.

Attempt at a General Method of Chemical Synthesis.—Raoul Pictet.—(See p. 273).

Fusion of Calcium Carbonate.—H. Le Chatelier.—The author finds that the melting-point of calcium carbonate is a little below that of gold, which confirms the accuracy of the determination of Hall towards the end of the last century.

The Molecular Weights of Sodammonium and Potassammonium.—A. Joannis.—The ammoniums studied may be represented by the formulæ N_2H_6Na and $N_2H_6K_2$.

A Propylamidophenol derived from Camphor.—P. Cazeneuve.—The author by successive transformations has succeeded in producing a propylamidophenol not yet described by setting off from camphor. The result confirms the presence in this substance of the propyl or isopropyl group.

The Colouring-Matter of Pollen.—G. Bertrand and G. Poirault.—Carotene, $C_{26}H_{38}$, is the colouring-matter of the yellow or orange pollens. It has probably a different physiological function in leaves and on the surface of pollen.

The Rotatory Power of Solutions.—M. Wyruboff.—The author concludes that the rotatory power of dissolved substances, like the rotatory power of crystalline bodies, is a phenomenon of a reticular order, which depends on the symmetry peculiar to the crystalline net. The particle which exists in solution retains this symmetry, and as this symmetry depends not alone on the chemical molecule, but also on the water of crystallisation (or whatever replaces it), there is no dissociation in the solution, nor, still less, separation into the electrolytic elements which are designated as ions.

On Vital and Chemical Fermentations.—Maurice Arthur and Adolphe Henri.—Sodium fluoride in the proportion of 1 per cent arrests instantly and finally vital fermentations without suspending the chemical fermentations. It thus enables us to distinguish the phenomena of these two groups.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 5th.—Society of Arts, 8. (Cantor Lectures). "The Generation of Light from Coal-Gas," by Prof. Vivian B. Lewes.

Medical, 8.30.

Society of Chemical Industry, 8. (1) "A New Form of Filter Press for Laboratory Use," by C. C. Hutchinson. (2) "The Production of Acetic Acid from the Carbohydrates," by Messrs. Cross and Bevan. (3) "Electrolytic Soda and Chlorine: The Present Aspects of the Question," by Messrs. Cross and Bevan.

TUESDAY, 6th.—Institute of Civil Engineers, 8.

Pathological, 8.30.

WEDNESDAY, 7th.—Society of Arts, 8. "The Chicago Exhibition, 1893," by James Dredge.

Geological, 8.

THURSDAY, 8th.—Royal, 4.30.

Royal Society Club, 6.30.

Mathematical, 8.

Institute of Electrical Engineers, 8. (Anniversary).

FRIDAY, 9th.—Physical Society, 5. "On Colour Vision" by W. B.

Croft. "On Magic Mirrors," by Professor S. P.

Thompson. "On Reflection from Diffusing Sur-

faces," by Dr. Sumpner.

Astronomical, 8.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1724.

ON THE PRESENCE OF MAGNETITE IN CERTAIN MINERALS AND ROCKS.*

By A. LIVERSIDGE, M.A., F.E.S.,
Professor of Chemistry in the University of Sydney.

THE following experiments to determine the amount of magnetite or of magnetic particles in minerals and certain rocks were made in consequence of the following statement in Bauerman's "Systematic Mineralogy," p. 298, 1881, viz.:—"Chrome iron and Franklinite are magnetic, but it is not certainly known whether this is a special property or caused by finely interspersed magnetite." Other writers, like Dana, simply state that the above minerals are magnetic, but do not make any comment as to whether the magnetic properties are inherent in the minerals named or due to enclosed magnetite; hence I thought it would not be altogether a waste of time to put the matter to the test of experiment. Accordingly I had some of the more common ferruginous and magnetic minerals crushed to a fine powder, sifted through a No. 60 sieve, and then acted upon by an electro-magnet under water. An electro-magnet was used because it is very difficult to brush off all the magnetic particles from an ordinary permanent bar or horse-shoe magnet, even when the armature is on. The magnet used lifted a weight of 18 ounces. A comparatively feeble one was purposely used, so as to attract and remove only those particles which would be attracted by a good ordinary permanent magnet; a powerful electro-magnet would not have been so suitable for the object in view.

The crushing was effected in a porcelain mortar, and finished in an agate one, to prevent access of particles of iron, which of course are always abraded from iron pestles and mortars. The non-magnetic matter can only be separated from the magnetic portions by repeated applications of the magnet and re-grinding, because a certain amount of the non-magnetic powder is apt to be entangled with the magnetic.

Inasmuch as hæmatite, Fe_2O_3 , is often somewhat magnetic, this was chosen as one of the first minerals to be tested for magnetite.

1. *Hæmatite*.—A dark compact red hæmatite; locality unknown, but probably from Elba. Acted on magnetic needle. The powder yielded—

	Grms.
Magnetic particles	10·15
Non-magnetic	56·80
	66·95

Or 15 per cent of magnetite.

2. *Hæmatite*.—Dark red botryoidal massive hæmatite, mixed with a little quartz. Frizenton, Cumberland, England. Yielded no magnetic particles.
3. *Hæmatite*.—The same as the last, but a softer variety. This also did not yield any magnetic particles.
4. *Micaceous Hæmatite*.—From the island of Tanna, where it is used by the natives for dusting over the body, for ornamental purposes, on account of its being in the form of bright glistening scales. This specimen is evidently of recent volcanic origin, and resembles the micaceous iron ore from Vesuvius and other volcanoes. It did not yield any magnetic particles.

5. *Micaceous Hæmatite*.—Locality unknown. Yielded traces of magnetic particles.

Weight of powder	18·7
Weight of magnetic particles ..	0·122
Percentage of magnetic particles	0·6

6. *Brown Hæmatite*.—Hydrated sesquioxide of iron. A hollow concretion; locality unknown, but probably from the Waianamatta shale: of a dark reddish brown colour. 51 grms. were crushed, but no magnetic particles obtained.
- 6A. *Stalactite* of hydrated sesquioxide of iron from Berrima, N.S.W. 26·62 grms. yielded only a trace of magnetic oxide.
7. *Dark Brown Hæmatite*.—Locality unknown. 22·5 grms. were treated, but no magnetic particles obtained.
8. *Brown Hæmatite*.—Compact and of a dark yellowish brown colour, from Kanderam, Baden. 44 grms. were treated, but no magnetic particles were obtained.
9. *Goethite*.—Yellow fibrous structure; from Kleinschmalkalden, Hessen. No magnetic particles were obtained from 43 grms.
10. *Goethite*.—Crystallised; from Lostwithiel, Cornwall, England. No magnetic particles.
11. *Goethite*, from Wallerawang, from irregular deposits in the sandstone. Yielded an almost black powder. No magnetic particles.
12. *Brown Hæmatite* from the quarry above the House of Correction, Hobart, Tasmania, where it occurs in thin crystalline plates, filling joints in the rock, which are about $\frac{1}{4}$ inch across. Free from magnetic particles.
13. *Brown Iron Ore*.—From Hungary. Compact dark yellow coloured. No magnetic particles from 58 grms. of the powder.
14. *Stalactitic Brown Hæmatite*.—Wallerawang, N.S.W., with bright black psilomelane-like coating. No magnetic particles.

Analysis.

Moisture	1·28
Combined water	12·04
Iron sesquioxide	73·60
Phosphoric oxide	0·12
Sulphur trioxide	0·06
Insoluble in acid	12·19
Loss	0·71

100·00

[See "Minerals of New South Wales," p. 96.]

15. *Brown Hæmatite*.—Dark brown in colour. No magnetic particles from 33 grms. of the powder.
16. *Brown Hæmatite*.—Wallerawang. Massive. Gave dark red-brown powder. May have been "roasted" in a bush fire. No magnetic particles.
17. *Brown Hæmatite*.—Wallerawang. Loose structure. Gave yellow-brown powder. No magnetic particles.
18. *Loose Brown Hæmatite*.—Wallerawang. No magnetic particles.
19. *Brown Hæmatite*.—Near Hobart, Tasmania. Dark brown colour; massive. Yielded light brown powder. No magnetic particles.
20. *Pea Iron Ore*.—Brown hæmatite. Locality unknown. No magnetic particles.
21. *Brown Hæmatite*.—New Guinea. Yielded a trace of magnetic particles.
22. *"Ironstone"*.—Brown hæmatite. Reigate, Surrey, England. No magnetic particles.
23. *Limonite*.—Clay Band, Wallerawang, N.S.W.: of a dark red-brown colour, looks as if it had been calcined; powder also red. A trace only of magnetic particles.

* From the Transactions of the Australasian Association for the Advancement of Science, Hobart Meeting, 1892.

24. *Limonite*.—Clay Band, Wallerawang, N.S.W. No magnetic particles.
25. *Brown Hæmatite*.—Brazil. Pseudomorphous after iron pyrites, auriferous. No magnetic particles.
26. *Ferrous Carbonate*.—Jamberoo, N.S.W. See "Minerals of New South Wales," p. 99. 35.1 grms. of powder yielded no magnetic particles. In another case 64 grms. of powder were also found to be free from magnetic particles.
27. *Iron Carbonate*.—A nodule from the coal measures, England. No magnetic particles.
28. *Iron Carbonate*.—A septarian nodule. No magnetic particles.
29. *Kraurite or Dufrenite*.—Green iron ore, hydrated iron phosphate. Ullersreuth, near Hof. No magnetic particles.
30. *Hornblende Schist*.—New Caledonia. Contained a little magnetite.
31. *Spinel* (Magnesium aluminate).—Ceylon. Red, transparent. No magnetic particles.
32. *Spinel*.—Elba. No magnetic particles.
33. *Spinel*.—Warwick, New York, U.S.A.; in large black octahedra. 32.102 grms. yielded 0.094 grm. of magnetite. Spinel crystallises in the same form as magnetite, and has the same general formula; hence the presence of magnetite, even in quantity, would not be surprising.
34. *Garnet*.—Franklin, New Jersey, U.S.A. Common iron alumina garnet of a brown-red colour. Did not yield any magnetic particles.
35. *Franklinite*.—Sussex Co., New Jersey, U.S.A. Strongly magnetic; 28.292 grms. yielded 9.131 grms. of magnetic particles, or 32.23 per cent.
36. *Chrome Iron*.—New Caledonia. Massive, black, with granular structure, but mixed with some steatite. When crushed the powder was of a grey tint, and did not yield any magnetic particles.
37. *Chrome Iron*.—New Caledonia. Massive, black. 95.7 grms. yielded 0.663 grm., or 0.69 per cent of magnetic particles.
38. *Chrome Iron*.—Wollomi, N.S.W. Black, massive; no visible foreign matter except a few particles of steatite. 190 grms. of powder only yielded a trace of magnetite.
39. *Pyrrhotine*, or magnetic pyrites, was found to be wholly attracted by the magnet, *i.e.*, its magnetic properties are apparently not due to the diffusion of particles of magnetite throughout its substance.
- 39A. *Pyrrhotine*, from Sala, Sweden, was also found to be wholly magnetic, except a small quantity of associated earthy gangue.
40. *Auriferous Hæmatite*.—Mount Morgan. 11.53 grms. were crushed and passed through a 60 sieve. No magnetite found.
41. *Jeweller's Rouge*.—Found to be free from magnetic particles.
42. Artificially prepared dry ferric hydrate was also found to be free from magnetic particles.
43. *Bornite*, or Purple Copper Ore.—Carn Brae Mine, Cornwall, England. Did not yield any magnetic particles.
44. *Iron Pyrites*.—Joshua's Creek, Taupo, New Zealand. The specimen is of recent origin, and in process of deposition round decaying wood and twigs in the stream of hot water supplying the baths. In parts it is black and powdery, but was found to be free from magnetic particles.
45. *Tinstone Conglomerate*.—Vegetable Creek, New England, N.S.W. This consists of rolled tinstone, quartz, &c., cemented together by iron oxide. 62.4 grms. of the powder was sent through a 60 sieve, but no magnetic particles were detected.
46. *Serpentine*.—Dark oily green colour, from Tasmania. 234 grms. yielded 8.4 grms. magnetic particles. Magnetic portion = 3.589 per cent. Another specimen of 50 grms. yielded 2.389 grms. of magnetite,
47. *Serpentine*.—Tasmania. Green, with visible specks of magnetite. 356.5 grms. gave 28.501 grms. of magnetic particles, or 7.99 per cent.
48. *Serpentine*.—New Caledonia. Dark brown, with veins of steatite and of magnetite. 212 grms. gave 5.92 grms. of magnetic particles, or 2.79 per cent.
49. *Serpentine*.—New Caledonia. Similar to last. 173.5 grms. gave 8.86 grms. of magnetic particles, or 5.10 per cent.
50. *Serpentine*.—New Caledonia. 26.2 grms. gave a trace only of magnetic particles.
51. *Serpentine*.—New Caledonia. 62.20 grms. gave 1.990 grms. of magnetic particles, or 3.19 per cent.
52. *Serpentine*.—New Caledonia. 25.7 grms. gave 3.67 grms. of magnetic particles, or 14.28 per cent.
53. *Serpentine and Asbestos*.—Tasmania. 24.0 grms. gave only a trace of magnetite. All the asbestos was separated before crushing.
54. *Serpentine*.—Lucknow, N.S.W. Very dark, almost black, with thin films of steatite. 33.80 grms. gave 7.773 grms. magnetic particles, or 22.99 per cent. A second specimen of the same, weighing 24.149 grms. yielded 6.08 grms. magnetite, or 25.13 per cent.
55. *Serpentine*.—Scotland. 28 grms. gave no magnetic particles.

All the serpentines examined acted upon a common five-inch magnetic needle, except Nos. 50, 53, and 55; No. 47 from Tasmania, and 49 from New Caledonia, were also distinctly polar. No nickel iron or awaruite was found in any of the serpentines.

Conclusion.

As far as the foregoing experiments are concerned, they show that in the specimens examined the magnetic properties of chrome iron, franklinite, spinel, garnet, some hæmatites, and other minerals and rocks are due to the presence of scattered particles of magnetite. In most cases the magnetic separated portion was further tested chemically, and proved to be magnetite, but it was not thought necessary to do this in every case. The pyrrhotine, however, appears to possess inherent magnetic properties.

THE QUANTITATIVE DETERMINATION OF RUBIDIUM BY THE SPECTROSCOPE.*

By F. A. GOOCH and J. I. PHINNEY.

(Concluded from p. 265).

It appears that within limits the presence of sodium in the flame increases the brilliance of the rubidium spectrum. The brightness of the lines is raised under the conditions to a maximum by the presence of sodium to 40 per cent of the weight of the rubidium, and increase in the amount of sodium does not further influence the brightness of the lines until the proportion of sodium to rubidium is as ten to one; or, speaking broadly, the difference between the dissociating effect of sodium upon the rubidium chloride (to which we attribute the effect noted) does not appear to be materially different whether one or a score of molecules of sodium chloride are present to one of the rubidium chloride. But when the proportion of sodium to rubidium much exceeds ten to one the glare of light diffused through the entire spectrum (though

Standard. Rubidium in a coil-full (1-50 c.m.)	Test solution. Rubidium in a coil-full with eighth-tenths of its weight of sodium.	Line of test compared with standard.
0.00066 m.grm.	0.00066 m.grm.	Brighter.
" "	0.00048 "	"
" "	0.00046 "	"
" "	0.00044 "	Equally bright.

* From the *American Journal of Science*, vol. xlv., Nov., 1892.

the sodium line itself may be cut off) begins to affect the vision, and as the increase advances ultimately extinguishes the rubidium lines utterly. The degree of increase in brilliance when the lines are at a maximum was determined by diluting the test-solution until a coil-full gave a line equally brilliant with that of the standard.

It is plain that at the maximum degree of brilliance the sodium is responsible for an increase of 50 per cent in the brightness of the lines.

The details of similar experiments in which potassium chloride was introduced into the flame with the pure rubidium chloride are given in the accompanying tabular statement.

Standard. Rubidium in a coil-full (1-50th c.m.) M.grm.	Test solution. Potassium in a coil-full. M.grm.	Comparison of lines of test taken by pairs.	Comparison of lines of test with standard.
{ 0'00066	0'00020	Slightly fainter.	Brighter.
	0'00040	Slightly brighter.	
{ "	0'00020	Fainter.	Brighter.
	0'00340	Brighter.	
{ "	0'00040	Equally bright.	Brighter.
	0'00066		
{ "	0'00040	Brighter.	Brighter.
	0'00340	Fainter.	
{ 0'00066	0'00066	Equally bright.	Brighter.
	0'00132		
{ "	0'00066	Brighter.	Brighter.
	0'00346	Fainter.	
{ "	0'00066	Brighter.	Brighter.
	0'00660	Fainter.	
{ "	0'00066	Brighter.	Brighter.
	0'01320	Fainter.	
{ "	0'00066	Brighter.	Brighter.
	0'02000	Fainter.	
{ "	0'00066	Brighter.	Brighter.
	0'02660	Fainter.	
{ "	0'00066	Brighter.	Brighter.
	0'03340	Fainter.	
{ "	0'00066	Brighter.	Brighter.
	0'03340	Invisible.	

From these results it appears that the presence of potassium produces an effect upon the rubidium lines similar to that of sodium; and, furthermore, the addition of 0'0004 m.grm. of potassium in the form of chloride to 0'00066 m.grm. of rubidium also in the form of chloride brings out the maximum brightness which is not materially changed by further addition of potassium up to about 0'0013 m.grm., but that the increase of the potassium to 0'0034 m.grm. results in diminution of brightness. In other words, it seems that a single molecule of potassium chloride has approximately the same dissociating effect upon the molecule of rubidium chloride in the flame as that brought about by a greater number, that the presence of potassium in the proportion of five parts to one of the rubidium begins to influence visibility unfavourably, that when this proportion rises to thirty to one of the elements (or twenty to one of the chlorides) the lines appear about as distinctly as if no potassium were present, and that an increase of proportion to fifty to one may bring about a sufficient glare of light to reduce the rubidium lines to invisibility. The degree of increase in brilliance due to the action of potassium when that element is present in proportions suitable to induce the maximum effect is shown in the following record.

Standard. Rubidium in a coil-full (1-50th c.m.), M.grm.	Test solution. Rubidium in a coil-full with its own weight of potassium. M.grm.	Line of test compared with standard.
0'00066	0'00066	Brighter.
"	0'00064	Brighter.
"	0'00057	Brighter.
"	0'00049	Brighter.
"	0'00044	Equally bright.
"	0'00040	Fainter.

It appears that the presence of 0'00044 m.grm. of potassium is capable of increasing the brilliance of the lines yielded by 0'00044 m.grm. of rubidium to an equality with the lines given by 0'00066 m.grm. of the pure salt; or, that the maximum increase of brightness amounts to 50 per cent.

It is evident, therefore, that means must be found to effect the separation of the rubidium from sodium and potassium, or of bringing test and standard to the same condition as regards the presence of these elements, before any reasonable degree of accuracy can be expected in the spectroscopic determination of rubidium as it ordinarily occurs in nature. The separation from sodium is easily accomplished by the conversion of the salts to the form of chloroplatinates; but for the quantitative separation of rubidium from potassium there is no good method known. The question as to the practical value of the spectroscopic reaction of rubidium for purposes of approximate quantitative analysis resolves itself into the problem as to whether by matching potassium lines as well as rubidium lines (following the method outlined in the determination of potassium in presence of sodium), and so bring the lines of test and standard equally under the influence of potassium, it is possible to make the comparison between the rubidium lines trustworthy. It was shown in the former paper that in matching solutions of potassium by means of the red line there is no difficulty; but the convenience of being able to use the spectroscope without re-adjustment throughout the entire experiment made it desirable to see whether the blue line of potassium might not serve sufficiently well in the comparison. It is hardly necessary to reproduce here in detail the evidence bearing upon this point, but we found as the result that the potassium may be determined by the use of the blue line with an error amounting to 10 per cent or 20 per cent, which, though far greater than that inherent in the use of the red line, admits of the attainment of determinations which should be accurate enough for the present purpose. We proceeded, therefore, to make a determination of rubidium in presence of potassium by the process referred to, the details of which are given in Experiment IV.

Experiment IV.

Standard solution containing { 0'0005 m.grm. rubidium }
to the coil-full. { 0'0015 " potassium }

Test solution contained 8 m.grms. rubidium and no potassium.

STEP 1.—*Preliminary Test for Rb.*—Test at 20 c.m.⁴ gave Rb line like standard.

STEP 2.—*Preliminary Matching of K Line.*—Test at 20 c.m.³ gave K line like standard when 1 m.grm. of K had been added.

STEP 3.—*Re-matching of Rb Line.*—Test at 35 c.m.³ gave Rb lines like standard.

STEP 4.—*Re-adjustment of K Line.*—Test at 35 c.m.³ gave K line like standard when 2 m.grm. were present.

STEP 5.—*Final Matching of Rb Line.*—Test at 35 c.m.³ gave Rb line like standard.

Rubidium found $35 \times 50 \times 0'0005 = 0'875$ M.grm.
" taken = 0'8
Error = 0'075 = 9'4 per cent.

It is evident that the percentage error is considerable, but inasmuch as the application of the process would naturally be to the determination of small absolute amounts of rubidium, we thought it desirable to go a step further to see whether means are at hand for separating large amounts of potassium from small amounts of rubidium with an approach sufficiently near to completeness to bring the potassium present within the limits allowed by the spectroscopic method. After some experimental

tion we fixed upon the simplest possible procedure, viz., the solution of the salts in the least possible amount of water, precipitation of the mass of potassium chloride by addition of alcohol, filtration, and the evaporation of the filtrate. In Experiments V., VI., VII., this mode of working was put to the proof. The amounts of rubidium indicated were dissolved in the form of the chloride in water, 0.1 grm. of potassium chloride was added, and the solution was evaporated and treated as described.

	Rubidium taken in the form of chloride. M.grms.	Potassium taken in the form of chloride. Grm.	Rubidium found. M.grms.	Absolute error. M.grm.	Percentage error. Per cent.
V.	1	0.1	0.8	0.2	20
VI.	2	0.1	1.7	0.3	15
VII.	1	0.1	0.9	0.1	10

The error of the process is manifestly large, and only roughly approximate results can be hoped for when large amounts of rubidium are dealt with; but, if the question is the estimation of only a few m.grms. of rubidium, it will appear, we think, in view of the fact that the only alternative is an indirect process, that even this great error is not absolutely prohibitive of what may be called fair determinations.

STANDARD IODINE SOLUTION:

A METHOD FOR ITS PREPARATION.

By H. L. PAYNE.

OF the methods proposed for determining sulphur in iron and steel, that first suggested by Elliott (*CHEMICAL NEWS*, xxiii., 61) merits attention on account of the ease and celerity of manipulation, as well as accuracy of the results obtained. This last point has been held in question by many chemists, but the record obtained by Lee S. Clymer, of the Crane Iron Co. (see *Four. Anal. Appl. Chem.*, June, 1892) places it on a par with those longer methods which have been considered highly accurate.

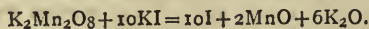
The essential feature of Elliott's method is the titration of the sulphur evolved as hydrogen sulphide, with a standard solution of iodine. Several methods are in use for the preparation of this solution of iodine.

The one given in Blair is tedious, in that it involves the use of two other standard solutions, one of potassium bichromate, and another of sodium thiosulphate, as well as an indicator solution of starch; moreover, the use of ammonium carbonate to retard the decomposition of the thiosulphate introduces a serious error in the titration, as has been pointed out by Topf (*Zeit. Anal. Chem.*, 1887, p. 137).

Mohr's method by weighing clear crystals of thiosulphate, and Fresenius's method by re-subliming and weighing the iodine direct, are both shorter and better.

A solution may also be made sufficiently exact for most uses by weighing 4 grms. iodine to the litre where 5 grms. of iron are taken for analysis, but like all the above methods it involves an uncertain error.

We have used for some time the following method and find it eminently satisfactory in every way. It depends upon the reaction between potassium permanganate and potassium iodide in solution:—



Sufficient acid, preferably sulphuric, is added to keep the manganese in solution and to render the fluid slightly acid. This reaction takes place in the cold and proceeds to completion even in dilute solutions. The strength of the permanganate solution being known, we can readily determine the amount of iodine liberated. One equivalent of potassium permanganate liberates 10 atoms of iodine, or oxidises ten atoms of iron. Hence, one atom of iron corresponds to one atom of iodine, and as one

atom of sulphur reacts with two atoms of iodine, two atoms of iron equal one atom of sulphur; or 128 grms. iron are equivalent to 32 grms. sulphur. Therefore the sulphur value of our permanganate solution will be $\frac{1}{16}$, or one-fourth of its iron value.

In preparing a standard iodine solution by this method, we are accustomed to proceed as follows:—

Take about 10 grms. potassium iodide in a litre flask; add 10 to 15 c.c. dilute sulphuric acid, and run in the calculated amount of potassium permanganate solution from a burette. Agitate a few moments until the reaction is complete and the solution clears, and dilute to the mark with water. A litre of such a solution can be prepared inside of two minutes in any laboratory having a standard permanganate solution constantly on hand, and there is, therefore, no necessity for keeping a standard iodine solution long enough to have it change materially.

A solution of permanganate such as is used in Emmerton's method for phosphorus titrates 6.141 grms. iron per litre, and of such a solution 325.7 c.c. will make one litre of iodine solution titrating 0.01 per cent sulphur per c.c. on 5 grms. iron or steel taken.

As an absorbent for the hydrogen sulphide, common white potash is to be preferred; potash purified by alcohol should be avoided. Dilute sulphuric acid may be used with advantage in acidifying the potash solution. The addition of methyl-orange to the starch solution in sufficient quantity to give a perceptible red colour to the solution to be titrated will, by turning colourless or a faint yellow on acidifying, indicate when an excess of acid has been added.—*Journal of Analytical and Applied Chemistry*, vi., No. 9.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 275).

ELECTROLYTIC SEPARATIONS.

Cadmium from Manganese.

Cadmium taken. Gm.	Manganese taken. Grm.	Cadmium found. Grm.	Free acid. C.c.	H ₂ O. C.c.	OH gas per min. C.c.	Time Hrs.	Diff. from theory. Percent.
1. 0.0497	0.0554	0.0425	35	75	0.8	16	—
2. 0.0497	0.0554	0.0440	35	75	1	16	—
3. 0.0497	0.0554	0.0498	25	75	2.7	17	+0.20
4. 0.0511	0.0554	0.0509	20	75	2.4	19	-0.39
5. 0.0511	0.0554	0.0697	5	150	2.7	18	—
6. 0.1022	0.1108	0.1098	20	75	2.5	17	—
7. 0.1022	0.1108	—	40	150	2.8	45	—
8. 0.0511	0.0554	0.0514	30	75	2.7	18	+0.58

In the preliminary experiments on manganese alone it was found that the presence of 20 c.c. of free acid was sufficient to prevent the deposition of any peroxide on the cathode, except in the very slightest traces; but the presence of cadmium in the solution, seemingly, had a contrary effect, as the presence of even 40 c.c. of acid failed to prevent the separation of traces of manganese on the negative pole 7. In 5, to which 5 c.c. of free acid had been added, the deposit of peroxide of manganese upon the negative pole was almost five times greater than in a solution of manganese to which no cadmium had been added, all the other conditions being the same. In all the above experiments the platinum dish was used as the anode, the platinum crucible serving as the negative electrode. In 1 and 2 the cadmium was not completely

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xlix., No. 136.

deposited. Traces of cadmium were found in 6 and 7. More or less manganese was found in all the deposits, but only in traces in the presence of more than 20 c.c. of free acid; 4 and 7 were very spongy; the others were slightly so at the periphery of the crucible, but adherent. The best results were obtained by fulfilling the conditions described in 3, 4, and 8; but to obtain a compact deposit of cadmium free from all traces of manganese, it is evident that the amount of free acid must be increased and the poles separated. Under these conditions a stronger current must be employed than that furnished by the battery of "crowfoot" cells, with which my experiments were carried on.

Zinc from Manganese.

Zinc taken.	Manganese taken.	Zinc found.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.0562	0.0554	—	30	90	2.9	17	—
2. 0.0562	0.0554	—	20	100	2.9	16	—

The dish served as anode, the crucible as cathode. Both were failures, the zinc being spongy and containing MnO₂, and not entirely precipitated.

Copper from Zinc.

Copper taken.	Zinc taken.	Copper found.	Free acid.	H O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.1074	0.0818	—	5	100	1.8	46	—
2. 0.1074	0.0818	—	5	100	1.2	17	—
3. 0.1074	0.1124	—	5	100	0.8	16	—
4. 0.1074	0.0818	0.1072	15	100	0.8	16	-0.18
5. 0.1074	0.0818	0.1073	20	100	0.8	17	-0.09
6. 0.0987	0.0818	0.0990	20	100	0.8	17	+0.30
7. 0.0987	0.0818	0.0984	20	100	0.6	15	-0.30
8. 0.1057	0.1006	0.1052	15	100	0.8	16	-0.47
9. 0.1057	0.1006	0.1061	15	100	0.8	18	+0.37
10. 0.1057	0.1006	0.1058	15	150	0.8	18	+0.09
11. 0.1057	0.1006	0.1059	20	150	0.8	19	+0.18
12. 0.1057	0.1006	0.1053	20	150	0.8	21	-0.37
13. 0.1057	0.1006	0.1060	20	150	0.8	16	+0.28

As will be seen from the above it was possible to separate copper free from zinc, except the slightest traces, by using a weak current in solutions to which 15—20 c.c. of free formic acid had been added. By employing stronger currents, or diminishing the amount of free acid, the copper was deposited admixed with considerable quantities of zinc. If the necessary precautions are observed no zinc will be deposited, and the copper will be compact and adherent.

Cadmium from Zinc.

Cadmium taken.	Zinc taken.	Cadmium found.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.1231	0.0818	—	15	100	0.2	17	—
2. 0.1231	0.0818	0.1229	30	100	0.8	19	-0.16
3. 0.1231	0.0818	0.1234	30	100	0.8	43	+0.24
4. 0.1231	0.0818	0.1226	35	100	1.25	16	+15.83
5. 0.1231	0.0818	0.1233	30	100	0.8	16	+0.16
6. 0.0492	0.0409	—	15	100	0.8	16	—
7. 0.0492	0.0409	0.0842	15	100	1.25	16	—
8. 0.0984	0.1026	0.0322	35	100	0.8	19	—
9. 0.0492	0.0409	0.0494	15	100	0.8	41	+0.40
10. 0.0984	0.1026	0.1735	35	100	1.25	17	—
11. 0.0984	0.1026	0.0722	35	75	0.8	17	—
12. 0.0984	0.1026	0.0982	25	125	0.8	18	-0.20
13. 0.0984	0.1026	0.0985	25	125	0.8	16	+0.10
14. 0.1004	0.1006	0.1001	25	125	1	48	-0.29
15. 0.1004	0.1006	0.0993	25	125	1	17	-1.09
16. 0.1004	0.1006	0.1000	25	125	1	17	-0.39
17. 0.1004	0.1006	0.1001	25	125	1	18	-0.29
18. 0.1004	0.1006	0.1008	25	125	1	20	+0.39
19. 0.1004	0.1006	0.0999	25	125	1	16	-0.49

The first seven determinations were made in a platinum dish weighing about 67 grms.; the remainder in a much larger dish weighing 117 grms. The results obtained with the latter were not as satisfactory as with the smaller dish (2, 3, 5), although a qualitative examination of the deposit and solution proved that the separation was complete (9, 12—19). The distance between the poles materially influences the results. In 6 the positive pole was in close contact with the dish; the cadmium contained zinc. In 9 the conditions were similar in all respects to the preceding, except that the distance between the poles was 2.5 c.m.; the deposit was free from zinc. With 0.2 c.c. OH gas per minute, only a small quantity of the cadmium was separated (1), the greater portion remaining in solution. With 1.25 c.c., on the other hand, the zinc was deposited as a dark grey coating upon the cadmium (7), even in the presence of 35 c.c. of free acid (10). In solutions containing 0.10 gm. of each metal a current of 0.8—1 c.c. HO gas per minute sufficed to secure a satisfactory deposit in the presence of 25 c.c. formic acid (12—19). With smaller quantities of metal (9) 15 c.c. of free acid was sufficient. The deposits in the above experiments were adherent and compact. There was no tendency to sponginess even in deposits containing large quantities of zinc.

(To be continued).

THE ARTIFICIAL PRODUCTION OF MINERAL SULPHIDES.

By H. N. WARREN, Research Analyst.

THE formation of sulphides by direct combination of the element sulphur with metallic substances usually affords little, if any, similitude to the natural or mineral form of the same compound. The reduction of sulphates by suitable means may be regarded as more imitative, but by employing as a reducing agent potassium sulphocyanide and bringing into contact with the same readily reducible oxides, the author has succeeded in imitating the natural sulphides to such a marked extent as to render detection impossible: or at other times producing in several cases entirely new compounds.

In the first instance, I will mention the action of KCNS upon litharge at a very low red heat; scaly litharge is almost immediately converted into galena, which, after washing, rivals in colour the native compound. The same substance, on raising the temperature to fusion under a layer of KCNS, breaks with an identical fracture, and possesses almost the same specific gravity as the dressed ore. Ferric oxide subjected thus to a continuous red heat yields brilliant pyrites, whilst at a still higher temperature the compound Fe₄S₃ is obtained, which may be also obtained by passing the vapour of CS₂ over metallic iron. Black oxide of manganese when treated with a large excess of KCNS and heated to bright redness, yields pyrolusite. Stannic oxide, as also the corresponding oxide of antimony, yields at high temperatures the ordinary sulphides; whilst at lower temperatures the golden sulphides have been obtained, possessing in all respects the full brilliancy of these compounds. Oxide of zinc treated thus yields a sulphide possessing very slight resemblance to the natural compounds, but, on the other hand, closely compares with the commercial pigment, though inferior as regards colour.

Phosphorescent sulphide of zinc has been already noticed on previous pages; it may therefore be of interest to state that several samples of zinc sulphide so prepared, after carefully cleansing the same from contaminated impurities, possessed this property in a marked degree.

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PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation and published in the *Transactions* :—

44. "Some Homonuclear Tri-derivatives of Naphthalene (Peridibromonaphthalene)." By R. MELDOLA, F.R.S., and C. H. DESCH (*Trans.*, 1892, 765).

It is shown that Prager's statement (*Ber.*, 1885, 2163) that the NH_2 group in 2-nitro-4-bromo-1-amidonaphthalene cannot be displaced by bromine by Sandmeyer's method is incorrect; and a description is given of the 1:4-dibromo-2-nitronaphthalene, and also of the corresponding chlorobromo- and iodobromo-naphthalenes; all three substances are described as crystallising in small ochreous needles melting at 117° . On reduction, they yield amines almost destitute of basic properties, which readily oxidise in air; their acetyl derivatives crystallise in white needles, bromido- β -acetonaphthalid melting at 235° , the chlorido-compound at 218° .

A lengthy footnote is appended to the paper, in which the conclusion arrived at by Armstrong and Rossiter (*Proc. Chem. Soc.*, No. 104, vii., 186), that when a mixture of ortho- and para-nitracetonaphthalid is brominated, the ortho-compound is alone attacked, is corroborated; and in which the interesting statement is made that one of the authors and F. W. Streatfeild have prepared peridibromonaphthalene from 1:1'-nitrobromonaphthalene: this new dibromonaphthalene melts at about 109° .

45. "A Method of Measuring the Vapour Pressures of Solutions." By THOMAS EWAN, B.Sc., Ph.D., and W. R. ORMANDY (*Trans.*, 1892, 769).

A condensation hygrometer for determining vapour pressures of solutions at ordinary pressures is described and figured. The hygrometer consists of a thin polished silver cup soldered to a stronger ring of brass, which in its turn is cemented into a glass tube by means of tinfoil and sulphur; the upper end of the tube is closed with a cork through which pass a thermometer and an open tube carried down below the surface of the ether placed in the silver bulb, a side tube near the top being connected with an aspirator in such a way that the amount of air passing through the ether is under the control of the observer. The hygrometer is suspended in a glass vessel containing the solution under examination; this consists of a cylindrical bulb with a long narrow neck, a narrow side tube through which the rod of a stirrer passes being sealed into the shoulder of the bulb. The temperature is determined at which dew first becomes visible on the silver bulb.

Results obtained with solutions of sodium and cupric chloride are given in the paper.

46. "The Hydrazines of Quinoline." By S. F. DUFON, B.A., D.Sc. (*Trans.*, 1892, 782).

A description is given of an improved method of nitrating quinoline, and of a variety of derivatives prepared from the ana-compound.

To nitrate quinoline, the nitrate prepared from 50 grms. is added in about five portions to 50 c.c. of strong sulphuric acid contained in a litre flask, 10 c.c. of fuming sulphuric acid ($d=2.0$) being poured in after each introduction of nitrate, the mixture being kept cool. The yield is very good, 200 grms. of ana- and 150 grms. of ortho-nitroquinoline having been obtained from 300 grms. of quinoline in one operation. A small quantity (equal to about 3 per cent of the quinoline taken) of a dinitro-hydroxyquinoline is formed; this substance very closely resembles trinitrophenol.

The compounds described are the ana-amine and hydrazine, the semicarbazide, pyruvic hydrazone, acetone hydrazone, benzaldehydehydrazone, and anquinoline-methylpyrazolone prepared from the hydrazine and anakinolone α -carboxylic acid.

It is pointed out that in the case of both ortho- and ana-derivatives, one remarkable feature common to both is the intense red colour of the mon-acid salts of the amine and hydrazine. The pyruvic hydrazone separates from an aqueous solution as a bright red crystalline precipitate differing from the corresponding ortho-compound by being soluble in water and by its vivid colour; this, however, changes to yellow on drying, with loss of water of crystallisation.

47. "The Origin of Colour. (IV.) Note on the appearance of Colour in Quinoline Derivatives and of Fluorescence in Quinine Salts." By HENRY E. ARMSTRONG (*Trans.*, 1892, 789).

Attention is directed to the fact that it could scarcely have been predicted that the anakinoline derivatives such as are described by Dr. Dufton would manifest colour, and it is argued that they are probably quinoid compounds: that the appearance of colour, in fact, is conditioned by the occurrence of an isodynamic change involving the passage from the "centric" structure of quinoline to the "ethenoid" structure of a quinone. Further, it is suggested that it may eventually prove to be possible to explain the fluorescence of certain salts of quinine by the application of a similar principle.

[Correction and Addendum.—It is stated in the foregoing note that "The ortho-derivatives described by Dr. Dufton, excepting the pyruvic hydrazone, apparently are colourless substances." This, as Dr. Dufton has pointed out to the writer, is not the case. The mistake—an entirely inexcusable one—appears to have been made owing to the absence from Dr. Dufton's paper describing the ortho-compounds of any reference to the colour of the acid salts of the amine and hydrazine; it is only incidentally, in the paper on the ana-derivatives, that he mentions that the intense red colour of the mon-acid salts of the amine and hydrazine is a remarkable feature common to both ortho- and ana-series; although an entry of this fact was originally made when my attention was first called to the work, in writing out the "note," the descriptions of the individual compounds were apparently alone consulted, and the incidental reference to the colour of the ortho-compound was consequently overlooked.

Although at present deprived of the forcible argument which the non-appearance of colour in the ortho-series would afford, I see no reason to abandon my contention that the coloured ana-compounds are of peculiar structure. Dr. Dufton's discoveries have, in fact, added greatly to the interest attaching to the study of quinoline derivatives, and it is necessary that the ortho-derivatives should be examined with special care. So many cases are now known in which substances long regarded as uniform definite compounds have proved to be composite that it is justifiable, in my opinion, to regard the ortho-derivatives with suspicion until their homogeneity has been placed beyond question.—H. E. A.]

48. "Dicarboxyglutaconic Acid." By S. RUHEMANN Ph.D., and R. S. MORRELL (*Trans.*, 1892, 791).

The action of phenylhydrazine on ethylic dicarboxyglutaconic acid and its benzyl derivative is shown to resemble that of ammonia, the final products being a pyrazolone derivative and ethylic malonate or benzylmalonate, the pyrazolone derivative being formed by condensation from the substituted amidoethylenedicarboxylate first produced. Phenylpyrazolone and several of its derivatives are described.

49. "Action of Nitric Acid on Anthracene." (II.) By A. G. PERKIN and J. E. MACKENZIE (*Trans.*, 1892, 865).

One of the authors has previously shown that compounds of anthracene with either ethylic or methylic nitrates are formed when solutions of anthracene in ethylic or methylic alcohol are treated with nitric acid. It is now shown that the corresponding propylic, isobutylic, and benzylic compounds may be prepared by using the appropriate alcohols; no corresponding product could be obtained from trimethylcarbinol, the action of nitric

acid on the solution of anthracene in this alcohol giving rise to nitrosoanthrone.

Under slightly modified conditions, the action of nitric acid on anthracene dissolved in isobutylic alcohol is found to give rise to a compound which the authors regard as nitroanthrone,—



this is converted into the isomeric nitroanthrol by treatment with alcoholic potash.

On treating anthracene dissolved in acetone (Kahlbaum's pure) with nitric acid, the compound of anthracene with methylic nitrate was produced in such quantity as to negative the assumption that it was derived from methylic alcohol present in the acetone: it would therefore seem probable that the acid acts on the acetone forming methylic nitrate and acetic acid. Using methylated ether carefully freed from alcohol, the compounds of anthracene with both ethylic and methylic nitrate were obtained.

50. "The Behaviour of Ethylene on Explosion with Less than its Own Volume of Oxygen." By B. LEAN, B.A., and W. A. BONE, B.Sc. (*Trans.*, 1892, 873).

After giving a brief account of previous observations, the authors describe a series of experiments in which mixtures of ethylene with its own or a less volume of oxygen were fired in a leaden coil. Their results are in agreement with those of Dalton, Kersten, and E. von Meyer, and show that, when fired with about its own volume of oxygen, ethylene eventually yields mainly carbonic oxide and hydrogen; but they have also observed that methane, acetylene, and carbon are produced.

The following are the tabulated results of the analyses:—

Composition of mixture.	C.	D.	E.	F.	G.
Ethylene	56.03	54.18	49.77	48.64	49.41
Oxygen	39.46	41.52	45.81	45.84	47.69
Nitrogen	4.51	4.30	4.42	5.52	2.90
Composition of product.	C.	D.	E.	F.	G.
Unsaturated hydrocarbons	5.53	3.77	2.78	2.14	—
Methane	5.96	3.77	2.52	2.55	1.01
Carbon dioxide ..	1.63	2.80	1.24	0.94	0.33
„ monoxide	38.85	44.84	47.79	46.53	49.11
Hydrogen	43.30	41.72	43.32	45.35	48.78
Nitrogen	5.16	3.10	2.35	2.49	1.01

Incidentally it is shown that oxygen is appreciably absorbed by fuming sulphuric acid, but that neither strong potash nor alkaline pyrogallol solution appreciably affects ethylene.

51. "The Lowering of the Freezing-points of Cadmium, Bismuth, and Lead when Alloyed with other Metals." By C. T. HEYCOCK, M.A., and F. H. NEVILLE, M.A. (*Trans.*, 1892, 888).

The authors have considerably extended the inquiry of which they have previously given a short account (*Proc. Chem. Soc.*, No. 88). A very large number of data are recorded in the paper. From these it is apparent that the "atomic fall," i.e., the ratio of the fall in freezing-point of the alloy below that of the pure solvent to the number of foreign atoms present per 100 of solvent, is independent of the concentration when the solution is dilute. As the concentration increases, a gradual change takes place, however, in the atomic fall value. In a few cases, such as that of gold in cadmium or tin, and of mercury in cadmium, there is an increase in the atomic fall as the concentration increases, but in most cases the reverse is true.

The various possible causes of change in atomic fall with increasing concentration are considered, and, after calling attention to the fact that Van 't Hoff's formula is strictly true only of infinitely dilute solutions, a formula applicable to finite concentrations is suggested; on the

assumption that the molecule of the substance in solution contains 1 atom, the different atomic fall values corresponding to different numbers of atoms of foreign metal per 100 of solvent are calculated, and it is then pointed out that on taking a general survey of the atomic falls given in the tables in the paper and comparing them with the molecular falls predicted by the theory of osmotic pressure, it is apparent, not only that the experimental numbers are identical in a great many cases with the theoretical fall produced by a monatomic molecule, but that the experimental numbers, while often lower, are never higher than the theoretical number. This is an important point in favour of the osmotic theory of solution, for this theory, whilst readily explaining a low atomic fall by the hypothesis of the dissolved molecule containing more than 1 atom, assigns a superior limit, corresponding to the state in which the molecules in solution contain each 1 atom of the dissolved substance. In presence of these numbers, it seems impossible to resist the conclusion that the process of dissolution consists essentially in the disintegration of the dissolved substance and its uniform diffusion through the solvent as a gas; in other words, that the "physical theory of solution" is correct. In some cases, however, for instance that of gold dissolved in cadmium and a few others, the authors have no doubt that the molecule in solution contains atoms of both metals.

52. "Isolation of a Compound of Gold and Cadmium." By C. T. HEYCOCK, M.A., and F. H. NEVILLE, M.A. (*Trans.*, 1892, 914).

The compound has the composition represented by AuCd, and is of a greyish silvery white appearance, like cadmium. It was prepared by alloying gold with cadmium and moderately heating in a vacuum so long as cadmium distilled away. The immediate interest of the compound is that it confirms the supposition advanced by the authors to account for the remarkable behaviour of gold and cadmium when dissolved in tin.

53. "The Resins of *Ficus rubiginosa* and *F. macrophylla*." By E. H. RENNIE, D.Sc., and G. GOYDER, jun. (*Trans.*, 1892, 916).

An account is given of the results of an examination of the resins of *F. rubiginosa* by De la Rue and Müller, contained in a paper published in the *Phil. Trans.* of 1860, and the somewhat different results of the authors are then recorded. They have separated a crystalline substance from both resins externally closely resembling De la Rue and Müller's product, but giving numbers for carbon about 3 per cent, and for hydrogen about 1 per cent higher; the numbers are most in accordance with the formula $\text{C}_{34}\text{H}_{56}\text{O}_2$. This substance is resolved by alkaline hydrolysis into acetic acid and a crystalline substance melting at 114°, of the formula $\text{C}_{32}\text{H}_{54}\text{O}$, very closely resembling the substance described by De la Rue and Müller, which they obtained in a similar way.

54. "The Hydrolytic Functions of Yeast." Part II. By JAMES O'SULLIVAN (*Trans.*, 1892, 926).

A further series of experiments on the hydrolytic activity of healthy yeast cells are described, the following being a summary of the conclusions arrived at:—

1. The hydrolytic action of yeast at ordinary temperatures (12° to 20° C.) follows the same course as that of a simple chemical interchange, and is not influenced by either air or carbon dioxide.

2. A time curve representing the action would correspond with that given for invertase under the most suitable conditions of acidity by O'Sullivan and Tompson (*C. S. Trans.*, 1890, lvii., 878). The rate therefore differs from that at which the alcoholic fermentation of yeast takes place, which would be represented by a straight line (Dumas, *Ann. Chim. Phys.* [3], 1874, 81; and A. J. Brown, *C. S. Trans.*, 1892, 384).

3. Any interference involving either an increase or a diminution of the natural acidity of the yeast cell diminishes its action. This is a very important matter, and

should always be considered when dealing with organisms or cellular membranes possessing the power of hydrolysing cane sugar. Dumas observed that both acids and alkalis interfered with alcoholic fermentation, and that in the case of alkalis the yeast possessed the power of overcoming the alkalinity, the liquid again becoming acid, and fermentation recommencing. It is found that a quantity of potassium hydrate which completely arrested the hydrolytic action of yeast for three to six hours was neutralised by the yeast in about twenty-four hours, the solutions eventually becoming acid and hydrolysis recommencing.

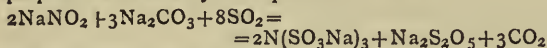
4. It is inferred from experiments on the effect of rupturing the cell on the velocity of the hydrolytic action, and also from the rate at which the change proceeds, that the whole of the invertase of the yeast cell comes into action as soon as the cane sugar is added to the yeast, and that it continues to act during the progress of the hydrolytic action.

5. The power which yeast possesses of producing alcoholic fermentation is not influenced by the yeast having first hydrolysed cane sugar, this being the case whether the hydrolytic action is brought about in the first instance in the presence of air or carbon dioxide.

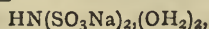
55. "Imidosulphonates." By E. DIVERS and T. HAGA (*Trans.*, 1892, 943).

The authors have obtained sodium imidosulphonate for the first time, and from sodium nitrite by a modification of Fremy's method of preparing the corresponding potassium salt (sulphamidate). The potassium salt is nearly insoluble in water, but the sodium salt is exceedingly soluble; and whereas the direct preparation of the former has proved to be uncertain and the yield unsatisfactory, the latter can be obtained from the nitrite almost without loss. Probably the potassium salt could be much more easily prepared than it has been were the here described modified process adapted to its production; but the sodium salt is a much more useful agent because of its solubility, and the potassium salt can at once be prepared from it by precipitating with potassium chloride.

Sodium nitrite and sodium carbonate (crystals) in the proportions shown by the equation—



are placed in a flask together with a little water and a rapid stream of sulphur dioxide is passed into the magma. The flask needs to be agitated, and during the latter part of the process to be kept cool. When neutrality is approached, the gas is to be passed in more slowly, and is to be stopped just when lacmoid paper is first permanently reddened. Two salts are now present in the liquor, sodium nitrilosulphonate and metasulphite, but in a few minutes hydrolysis of the nitrilosulphonate sets in, giving disodium imidosulphonate and acid sulphate, and the latter acts on the metasulphite, forming sulphurous acid and disodium sulphate. By thus taking up the sulphuric acid, the metasulphite entirely prevents subsequent hydrolysis of the imidosulphonate into amidosulphonate. After expelling sulphur dioxide by a rapid current of air, a little sodium carbonate is added to make the liquor slightly alkaline, and enough of the water is evaporated off at a gentle heat. On cooling to near 0° , most of the sulphate crystallises and can be removed. The concentrated mother-liquor affords hard, brilliant crystals, of almost pure imidosulphonate; from its mother-liquor more sulphate and imidosulphonate can be alternately separated. The imidosulphonate can be safely re-crystallised from slightly alkaline warm water or by cold evaporation. It forms large, rhombic prisms of the composition—



feebly acid to litmus, which only very slowly lose water in a vacuum.

Like the potassium salt, disodium imidosulphonate is not precipitated by many of the ordinary agents, because

nearly all other imidosulphonates corresponding to it are soluble. It, however, affords precipitates with sodium hydroxide, potassium chloride or nitrate, barium hydroxide, strong ammonia-water, basic lead acetate, and mercuric and mercurous nitrates; most of these act also on the dipotassium salt. Sodium hydroxide precipitates trisodium imidosulphonate; and the same salt is formed by evaporating the disodium salt with sodium carbonate, or with sodium acetate if the evaporation is repeated. Potassium chloride precipitates the dipotassium salt. Ammonia precipitates a sodium ammonium salt, and also when the solutions are very concentrated triammonium imidosulphonate; but in presence of other sodium salts, nitrate or chloride, ammonia precipitates pure trisodium imidosulphonate, leaving ammonium nitrate or chloride in solution. Baryta-water gives a barium sodium imidosulphonate.

Trisodium imidosulphonate, $\text{NaN}(\text{SO}_3\text{Na})_2 \cdot (\text{OH}_2)_{12}$, crystallises in thin plates, sparingly soluble in cold water, freely soluble in hot water. It is a very stable salt, easy to prepare and to preserve for unlimited periods. It is an alkaline salt, and when neutralised with sulphuric acid furnishes a solution from which the disodium salt can be crystallised out. In a vacuum the crystals lose only eleven mols. of water; the other one can be expelled by heat almost completely. A number of other imidosulphonates of corresponding composition, often double salts, can be prepared from the trisodium salt by precipitation; ammonium imidosulphonates can be also prepared from it, through the intermediation of the barium hydrogen salt, or the basic lead salt, or the silver salt.

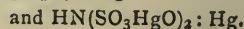
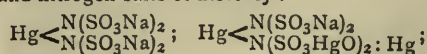
Berglund, eighteen years ago, established the fact that diammonium imidosulphonate is Rose's parasulphat-ammon, still described in the latest English text-books (Ramsay, Mendeléeff) as ammonium amidosulphonate. The authors find that dry diammonium imidosulphonate, an anhydrous salt, combines with dry ammonia to form anhydrous triammonium imidosulphonate, and that this is Rose's sulphatammon. They have also prepared in the wet way a triammonium imidosulphonate with 1 mol. of water, isomorphous with tripotassium imidosulphonate.

Barium imidosulphonate is precipitated as a voluminous matted mass of microscopic, fibrous crystals, in appearance like an organic salt. Barium hydrogen, barium ammonium, barium sodium, barium potassium imidosulphonates are all crystalline salts. Of the double calcium salts, the sodium compound may be mentioned as forming stellate groups of thick, often very brilliant, prisms.

Besides a very soluble, unstable lead hydrogen salt, a prismatic tri-hemihydroxy-lead salt, $(\text{HOPb})_3\text{N}(\text{SO}_3)_2$, and a tetra-lead salt, $\text{HO}(\text{HOPb})_4\text{N}(\text{SO}_3)_2$, which are both insoluble, may be obtained. No double lead salts can be prepared; the hydrogen salt is known only in solution.

The interaction of trisodium imidosulphonate and silver nitrate is specially remarkable for giving in succession three strikingly different precipitates:— $\text{AgNa}_2\text{N}(\text{SO}_3)_2$, in the form of fibrous, pale yellow crystals; $\text{Ag}_2\text{NaN}(\text{SO}_3)_2$, a sparkling, white "sand" of microscopic, hexagonal crystals, all detached; and $\text{Ag}_3\text{N}(\text{SO}_3)_2$, a white precipitate, drying on the tile to chalk-like masses. The relation in composition of these three silver salts is also interesting for its rare, if not exceptional, character.

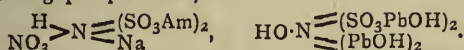
The following double mercury salts are well-defined compounds which have been examined in detail because of their interest as being at the same time sulphonic and nitrogen salts of mercury:—



Neither a single mercury imidosulphonate nor any mercurous salts can be prepared. Berglund's belief in the existence of a specially stable mercury imidosulphonic acid is not confirmed by the authors' observations, for although mercury dipotassium imidosulphonate readily

exchanges its potassium for barium and other metals, it keeps its potassium and exchanges its mercury for hydrogen when treated with nitric acid; and, besides, mercury hydrogen imidosulphonate is apparently less stable than imidosulphonic acid itself.

Diammonium imidosulphonate forms a double salt with sodium nitrate, and so does the dipotassium salt. The existence of these compounds and of the pentahydroxy-tetra-lead salt, and the retention of 1 mol. of water by the trisodium salt left in a vacuum-desiccator seem to show that imidosulphonates preserve some of the power of ammonia to unite with acids and salts, the nitrogen becoming quinequivalent, thus:—



The effect of heating ammonium and potassium imidosulphonates has been examined by previous workers, but their observations are defective. Diammonium imidosulphonate melts and boils near 357°, and flows back almost unchanged. Violent ebullition for an hour has little effect if moisture be rigorously excluded. But the salt decomposes to a small extent like the potassium salt. Dipotassium imidosulphonate is decomposed only at the softening point of good soft lime glass into potassium sulphate, ammonia, sulphur dioxide, and nitrogen. The carefully dried disodium salt behaves similarly. The trisodium salt at the same high temperature gives sodium sulphate, sulphur, and nitrogen. Lead, silver, and mercury salts are somewhat more easily affected by heat; in their case, besides products such as are above enumerated, mercury and even its sulphide, silver and silver sulphide, lead sulphide and sulphite are among the products. The barium salt decomposes explosively.

Anhydrous imidosulphonates of potassium or sodium, alone or with other metals, when heated to about 130° and upwards in ordinary air, slowly increase in weight and become acid, being hydrolysed by the atmospheric moisture. This fact is the more interesting in that at about the same temperature amidosulphonates, heated in dry air or in a vacuum, give off ammonia and become imidosulphonates, as was first observed by Berglund.

ADDENDUM.—*Oxyamidodisulphonates*. Soon after the appearance of the authors' last paper (*Journ. Chem. Soc.*, lv., 765), which treated of *oxyamidodisulphonates*, Dr. Raschig wrote to request them to state on his behalf that he agreed with their account of the decomposition of these salts by caustic alkali, and wished to withdraw his own statement which had been based on qualitative observations only.

56. "Modification of Beckmann's Boiling-point Method of Determining Molecular Weights of Substances in Solution." By JOJI SAKURAI.

The great experimental difficulty affecting Beckmann's well-known method is the exact determination of the boiling-points. A thermometer dipped into a boiling liquid always gives irregular readings, but this difficulty may be completely overcome by the method already described by the author in his paper on "The Determination of the Temperature of Steam Arising from Boiling

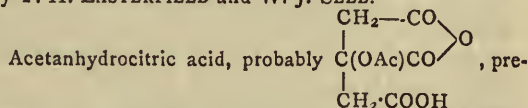
Salt Solutions" (*C. S. Trans.*, 1891), which consists in passing a current of the vapour of the solvent into the boiling liquid, the amount of the vapour thus passed in being regulated by the height of the lamp. The degree of constancy of the temperature attained in this manner by the boiling liquid is really astonishing, a most delicate thermometer capable of showing 1-1000th of a degree remaining almost stationary.

The apparatus used is of the simplest construction and can be set up by any one with materials commonly found in all chemical laboratories. Another advantage is that the boiling-point of the solution is ascertained just before its composition is determined, the connection between these properties being, therefore, rendered more certain than in the case of Beckmann's method.

The accompanying Table gives an example of the results obtained.

The author confirms the statement, first made by Beckmann, that the difference in colour of iodine when dissolved in ether and in carbon bisulphide is not due to a difference in the state of its molecular aggregation, the numbers obtained for the molecular weight of iodine, when dissolved in carbon bisulphide (247.1—261.9) agreeing with those contained in the Table (255.0—261.6). Beckmann's view that the molecular magnitude of sulphur in carbon bisulphide solution is represented by the formula S₈ has also received a striking confirmation in the author's hands, the numbers he obtained varying only between 252.3 and 254.9 (S₈=256).

57. "Anhydro-Derivatives of Citric and Aconitic Acids." By T. H. EASTERFIELD and W. J. SELL.



pared from anhydrous citric acid and acetic chloride, crystallises from ether in groups of short prisms melting at 115°; it decomposes at higher temperatures, yielding citraconic anhydride if distilled under ordinary pressure, and itaconic anhydride when distilled under reduced pressure (30 m.m.). It yields acetylcitric acid on hydrolysis; aniline converts it into citrodianilic acid; when hydrolysed by alcoholic potash it affords aconitic acid, the method being probably the best yet devised for the preparation of this acid. Ammonia converts acetanhydrocitric acid into citrazinic acid.

Aconitic anhydride may be prepared by boiling aconitic acid with excess of acetyl chloride; it crystallises out in colourless deliquescent octahedra. On treatment with ammonia it affords citrazinic acid.

The authors were unable to obtain citrazinic acid from tricarballylic anhydride and ammonia, and point out that the formation of this acid from citric ethereal salts is probably largely dependent on the easy formation of an ethenoid union.

58. "Disubstituted Semithiocarbazides." By AUGUSTUS E. DIXON, M.D.

In two former papers (*Trans.*, 1889, 302; and 1890, 257) the author gave a short account of some members of

Solvent: Ethyl Ether.

Lat. Ht. Vap.=90.1 (Regnault, 1862); b. p.=34.9° C. $\frac{0.02T^2}{W} = 21.0$.

Substance.	B. p.			g solution.	g substance.	g solvent.	g substance per 100 g solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution.	Rise.						
Salicylic acid, C ₆ H ₄ OH·CO ₂ H=138	1.013	1.397	0.384	6.9880	0.1733	6.8147	2.543	139.1	+0.8
" "	1.337	1.661	0.324	7.2700	0.1591	7.1109	2.237	145.0	+5.1
" "	0.986	1.236	0.250	7.1384	0.1174	7.0210	1.672	140.4	+1.7
Naphthalene, C ₁₀ H ₈ =128. . . .	0.739	1.464	0.725	7.2743	0.3128	6.9615	4.493	130.1	+1.7
" "	1.038	1.541	0.503	7.0014	0.2143	6.7871	3.159	131.9	+3.0
" "	1.275	1.542	0.267	7.0232	0.1112	6.9120	1.609	126.6	-1.1
Iodine, I ₂ =254	1.295	1.615	0.320	7.1600	0.2678	6.8922	3.886	255.0	+0.4
" "	1.098	1.302	0.204	7.2838	0.1796	7.1042	2.528	260.2	+2.4
" "	1.174	1.255	0.081	6.9250	0.0692	6.8558	1.009	261.6	+3.0

the class of semithiocarbazides, principally with reference to the isomerism there shown to exist amongst the disubstitution derivatives. The study has since been continued, but the publication of a paper dealing with such compounds was deferred until further investigation should be made regarding a phenomenon which was frequently observed, viz., the apparent existence, for a given semithiocarbazide of two different melting-points. A communication has, however, just appeared in the *Berichte* (1892, 3098), in which this latter subject is especially dealt with; the author, therefore, desires to record, without further delay, the experimental results which he has already obtained.

Paratolylphenylsemithiocarbazide (from p -ToNCS and $\text{PhNH}\cdot\text{NH}_2$) occurs as a colourless crystalline mass, sintering at 149° ; or in vitreous prisms, melting at 173° to 174° (uncorr.).

Phenylparatolylsemithiocarbazide (from PhNCS and p -ToNH $\cdot\text{NH}_2$) occurs as a crystalline mass, sintering at 117° , and convertible, by repeated crystallisation from boiling alcohol, into feathery needles, becoming electrical on friction and melting at 172° (uncorr.). This and the preceding pair are doubtless identical with compounds described (*loc. cit.*) by Marckwald.

Orthotolylparatolylsemithiocarbazide, when prepared at a moderate temperature from o -ToNCS and p -ToNH $\cdot\text{NH}_2$, melts at 130 – 131° , immediately resolidifying; on further heating, it again melts at 162 – 163° . The compound of m. p. 162 – 163° is directly obtained by combining the constituents in boiling (alcoholic) solution.

Paratolylorthotolylsemithiocarbazide, prepared from p -ToNCS and o -ToNH $\cdot\text{NH}_2$, forms vitreous prisms melting at 141 – 142° (uncorr.). The formation of a compound having a lower melting-point was not observed.

Diorthotolylsemithiocarbazide.—Brilliant colourless octahedra, melting at 148 – 149° (uncorr.).

Diparatolylsemithiocarbazide.—If prepared in gently-warmed alcoholic solution, forms aggregates of flattened crystals, melting at about 125° , but at once resolidifying and then melting at or near 153° . By mixing boiling alcoholic solutions of the constituents, the substance is obtained in pointed prisms melting at 153 – 154° (uncorr.).

Alphanaphthylphenylsemithiocarbazide (from α -NapNCS and $\text{PhNH}\cdot\text{NH}_2$).—Brilliant vitreous needles, melting at 183° (uncorr.). Isomeric with Freund's (*Ber.*, xxiv., 4190) phenyl- α -naphthyl derivative melting at 135° .

Phenylbetanaphthylsemithiocarbazide, prepared from PhNCS and β -NapNH $\cdot\text{NH}_2$, forms pearly needles, melting at 184 – 184.5° (uncorr.). According to Freund (*loc. cit.*) this substance melts at 202° .

Betanaphthylphenylsemithiocarbazide, prepared from β -NapNCS and $\text{PhNH}\cdot\text{NH}_2$, crystallises in silvery needles, melting at 190 – 191° (uncorr.).

Benzylphenylsemithiocarbazide.—White flexible prisms; m. p. 115 – 116° (uncorr.). On heating in alcoholic solution with a trace of chlorhydric acid, the m. p. rises to 163° .

Benzylparatolylsemithiocarbazide.—Shining flattened prisms; m. p. 120 – 121° (uncorr.).

59. "Studies on the Interaction of Bromine and Toluene. Preparation and Properties of Ortho- and Para-bromotoluene, and of the Dibromotoluenes Derivable therefrom. Ortho- and Para-bromotoluenesulphonic Acids." By A. K. MILLER, Ph.D.

It is shown that parabromotoluene affords two dibromotoluenes, viz., orthoparadibromo- and metaparadibromotoluene, the latter being the major product; orthobromotoluene yielding orthoparadibromotoluene as minor product, together with the orthometa-derivative containing the bromine atoms relatively in the para position. Parabromotoluene also yields some 1:2:4:5-tribromotoluene ($\text{Me}=1$), which appears to be derived from the 1:2:4-di-derivative.

60. "Note on the Constitution of Nevile and Winther's Orthotoluidinesulphonic Acid, and on the Acids Formed

by Sulphonating Orthochloro- and Bromo-toluene." By W. P. WYNNE, D.Sc.

A comparison of the chloro- and bromo-acids obtained by Sandmeyer's method from Nevile and Winther's orthotoluidinesulphonic acid with those formed from orthochloro- and orthobromo-toluene by sulphonation has established their identity. Nevile and Winther gave reasons for assigning to their acid the constitution $[\text{Me}:\text{NH}_2:\text{SO}_3\text{H}=1:2:5]$, but further evidence seemed desirable in view of the nature of their proof. The metabromotoluidinesulphonic acid formed from Nevile and Winther's acid by careful bromination was converted by Sandmeyer's method into the corresponding dibromotoluenesulphonic acid, and the sulphonic radicle was eliminated from the acid by hydrolysis with phosphoric acid in a current of superheated steam; the resulting dibromotoluene was identified as the 1:2:3-derivative, since it melted at 30 – 31° , and its nitro-derivative at 59° .

It hence follows that the bromotoluidinesulphonic acid has the constitution $[\text{Me}:\text{NH}_2:\text{Br}:\text{SO}_3\text{H}=1:2:3:5]$, and Nevile and Winther's acid that assigned to it by them.

61. "The Action of Iodine on a Mixture of Sulphite and Thiosulphate." By ARTHUR COLEFAX, M.A., Ph.D.

This paper has reference to Spring's contention, advanced in his recent note in the *Proceedings* (1892, 91), that although it is true, as the author had asserted, that no trithionate is formed by the action of iodine on a mixture of sodium sulphite and thiosulphate, trithionate is produced if potassium salts are used in place of sodium salts. It is shown that trithionate is not produced by the action of iodine either on the potassium or sodium salts, and that the formation of trithionate is due to the occurrence of a secondary interaction of tetrathionate and sulphite, which takes place when the iodine acts slowly, as it does, especially when used in the solid state. It is also shown that when iodine acts on a solution containing both sulphite and thiosulphate of potassium or sodium, present in molecular proportions, it oxidises the sulphite only slightly more quickly than it converts the thiosulphate into tetrathionate.

62. "The Methylic Salts of Camphoric Acid." By JAMES WALKER, Ph.D., D.Sc.

The author has prepared the dimethyl and the two methyl hydrogen salts of camphoric acid, and finds their properties to be in the main the same as those of the compounds described by Brühl and Braunschweig and by Haller. Orthomethylic sodic camphorate may be obtained by adding 1 mol. prop. of powdered camphoric anhydride to a cold solution of 1 at. prop. of sodium (1 mol. prop. sodium methoxide) in methyl alcohol; the corresponding hydrogen salt may be prepared by acidifying the sodium salt. If 1 mol. prop. of methyl iodide be added in addition, and the mixture be heated for twenty-four hours at 100° , dimethylic camphorate is formed. The author succeeded in obtaining the allomethylic hydrogen camphorate in a measurable form by crystallisation from metaxylene. The "dissociation" constant of the ortho-compound is 0.0008, of the allo-compound 0.000975, which are nearly equal and not far removed from half of that of camphoric acid, viz., 0.00225. These values correspond with the assumption that camphoric acid is a dicarboxylic acid, and are at variance with the formula proposed by Friedel.

The Chemical Society.—We wish to draw special attention to the fact that an Extra Meeting of the Chemical Society will be held at 8 p.m. on Tuesday, December 13th, the Anniversary of the death of Stas. A paper, specially prepared for the occasion by Prof. J. W. Mallet, F.R.S., entitled "Jean Servais Stas, and the Measurement of the Relative Masses of the Atoms of the Chemical Elements," will be read and discussed.

NOTICES OF BOOKS.

Practical Physics: an Introductory Handbook for the Physical Laboratory. By W. F. BARRETT, F.R.S.E., M.R.I.A., and W. BROWN. Part I. "Physical Processes and Measurements, the Properties of Matter." 12mo., pp. 284. London: Percival and Co., 1892.

THE authors in their preface quote the important dictum of Prof. Huxley, that in Science "mere book-learning is a sham and a delusion." They eulogise the value of practical physics as mental discipline, and they applaud the "enlightened policy of the Director of the Science and Art Department" for doing what we should consider a simple duty.

It is noted that "the number of existing text-books in practical physics is still very small compared with the many admirable handbooks on practical chemistry." The authors surely do not consider this number of works to be any advantage! The introductory chapter, they think, may be objected to as going beyond the proper boundary of physics, and they suggest that teachers who are of this opinion may begin with Chapter II. The next chapters up to V. are intended for general students. Chapters VI. to IX. are more especially adapted for those who have the engineering phase of the subject in view, and the remaining chapters are intended for those taking up pure physics or chemistry.

In Chapter I. the authors "take up the hatchet" against the hypothesis of the evolution of atoms, which, in the words of Sir John Herschel and Prof. Clerk Maxwell, present the appearance of "manufactured articles." They omit, however, to show the raw material from which they have been manufactured. The idea of their being eternal and self-existent is more decidedly excluded by considerations drawn from their relative abundance and distribution.

Messrs. Barrett and Brown admit that temperature is not included "in any authorised way" in the three fundamental units—space, time, and mass. They do not deny the possibility of space of n dimensions. The more practical portion of the book, if duly taken in conjunction with experiments, will prove very useful for teachers and students.

Manual of Qualitative Blowpipe Analysis and Determinative Mineralogy. By F. M. ENDLICH, S.N.D., Mining Engineer and Metallurgist. 8vo., pp. 456. New York: The Scientific Publishing Co., 1892.

THE attention paid to blowpipe analysis in the United States is almost as striking as its comparative neglect in Britain. We might almost wonder that there should be an opening for the present work in face of the existing American version of Plattner. Dr. Endlich, however, does not enter upon the use of the blowpipe in quantitative operations. He devotes some pages to the application of the spectroscopy in qualitative analysis, which he considers should be employed wherever possible. Its utility is, of course, not to be questioned. He gives also instructions for the examination of paints, pigments, and wall-paper. A number of methods for the determination of minerals are introduced which do not turn on the use of the blowpipe, but which will be found exceedingly useful. The general instructions for qualitative analysis are highly judicious, and speak of the habit of prolonged and careful observation. In Section 210 we observe a typographical error, the acidity of water on the absorption of sulphurous acid being said to produce *sulphides*.

In the table of atomic weights we find platinum given as higher than gold, the former being stated as = 196.7, and the latter as 196.2. In fine, though this work is not likely to supersede Plattner, it will prove a very useful adjunct, and it may be accordingly recommended to all chemists who practise blowpipe analysis, and of course to all mineralogists and metallurgists.

CORRESPONDENCE.

THE DETERMINATION OF PHOSPHORIC ACID IN BASIC SLAGS.

To the Editor of the Chemical News.

SIR,—I read with interest Dr. Adolf Jolles' criticism upon the Albert method of determining phosphoric acid in basic slags, which appeared in the CHEMICAL NEWS, vol. lxxi., p. 262.

Having previously investigated the errors specifically shown by Dr. Jolles in his paper, I arrived at the same conclusions as himself, and communicated the results to others during the past year. I therefore feel sure of your permission to make a few comments upon the subject-matter of the German chemist's contribution.

I have no desire to make any untoward remarks upon Dr. Jolles' assertion, relative to the danger of missing some phosphoric acid through opening up basic slags with sulphuric acid, at the same time it would be rather a matter of surprise to find anyone experienced in the analyses of fertilisers adopting sulphuric acid as the solvent for these slags, which his comments seem to indicate.

Dr. Jolles rightly points out that the evaporation of the acid solution of slags to the consistency of a gelatinous paste is insufficient to effect the complete separation of silica. As a result of experiments made, I found that some silica invariably remains in solution, and that it was subsequently co-precipitated with the phosphoric acid, giving too high results as now described by him. It was therefore found necessary to evaporate the acid solution to absolute dryness in order to effect a perfect separation of silica, in some cases two evaporations being found preferable.

The condemnation of the Joulie volumetric method of estimating P_2O_5 by Dr. Jolles on account of the uncertain character of the prussiate indicator is justifiable, and I may say that I abandoned the use of this method several years ago when analysing raw phosphatic materials, finding it only possible to obtain approximate results even when the method was applied under conditions as far constant as possible as regards volume of liquid, quantities of salts present, &c.

The modification proposed by Dr. Jolles in the application of the Joulie method in the analysis of basic slags is requisite so far as regards too high figures, resulting from the incomplete separation of silica; but apart from this source of error, there is, I submit, reason to differ with Dr. Jolles in prescribing the Joulie method for the gravimetric determination of P_2O_5 . The writer has frequently observed the weight results obtainable by this method to be too high, and has found it to be untrustworthy for the accurate determination of phosphoric acid.—I am, &c.,

ALFRED FIRBY, F.I.C.,
Manure Analyst, &c

10, Infirmary Street, Leeds, Nov. 29, 1892.

DENSITY AND MOLECULAR WEIGHT.

To the Editor of the Chemical News.

SIR,—In making some calculations a few days ago, I noticed the following coincidence, which I take the liberty of communicating to you in case it might be of interest.

A gas doubles its volume when raised from 0° to 273° C.; greatest density of water is at 3.9° C. Now $273 \div 3.9 = 70$ exactly; molecular weight of water = 17.96. Now $17.96 \times 3.9 = 70.04$, or $(3.9) \times 17.96 = 273.18$, which is also freezing-point of water in absolute temperature. (Temperature of greatest density)³ $\times$ molecular weight = 273.18 .—I am, &c.,

H. TREHERNE.

THE VOLATILE FATTY ACIDS OF BUTTER.

To the Editor of the Chemical News.

SIR,—Will you grant me space in your next issue to deny Mr. Johnstone's statement that I made an arithmetical mistake in my "Note" (CHEMICAL NEWS, vol. lxi., 235)? My figures are all correct to the decimal to which they are calculated.—I am, &c.,

H. DROOP RICHMOND.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed:

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 21, November 21, 1892.

Action of Piperidine upon the Haloid Salts of Mercury.—Raoul Verdol.—The author has prepared piperidine chloromercurate and the corresponding bromomercurate, cyanomercurate, and iodomercurate. The mercurous chloride, bromide, and iodide, if treated with piperidine, are decomposed into metallic mercury and mercuric salts, which enter into combination with the base. If these results are compared with those previously obtained with ammoniacal gas and piperidine, it is found that at ordinary temperatures the haloid salts of mercury, if treated with an excess of these compounds, yield compounds containing 2 mols. of base to 1 mol. of salt of mercury.

Exchanges of Carbonic Acid and Oxygen between Plants and the Atmosphere.—Th. Schloesing, jun.—The question which the author undertakes to answer is what, for an entire plant during the whole term of its existence, is the result of the exchanges of carbonic acid and of oxygen which it effects with the ambient air? How much does it evolve for a given volume of carbonic acid which has disappeared? The experiments are described but no conclusions are reached.

Researches on the Method of Production of Perfume in Flowers.—E. Mesnard.—The essential oil is generally localised in the epidermic cellules of the upper surface of the petals or the sepals. It may exist on both surfaces, especially if the parts of the flower are completely hidden in the bud. The lower surface generally contains tannin or pigments derived from it. 2. Chlorophyll seems in every case to give rise to the essential oil. The transformation is easily understood if we admit, as it is now generally done, that the parts of the flower are merely leaves modified for a new function. The chlorophyll is thus turned away from its object, and is transformed either into persistent tannin derivatives or into essential oils. 3. The development of the perfume of the flower is not perceptible until the essential oil is sufficiently liberated from the intermediate products, and it is present to some extent in an inverse proportion to the production of tannin and of pigments in the flower. This will explain why flowers with green petals have no odour; why white or rose-coloured flowers are most frequently odoriferous; why the Compositæ, which are rich in tannin, have their well-known disagreeable odour.

MISCELLANEOUS.

Diaries for 1893.—We have received from Messrs. Cassell and Co., Ltd., sole publishers of the original series of Letts' Diaries, a selection of the Rough and Commercial, and Office and Pocket Editions of Diaries for the ensuing year. These useful adjuncts to the desk and library are so well known that detailed comment is super-

fluous. We notice an addition to the No. 31 Rough Diary and the No. 8 Office Diary—the books most generally useful for offices—which cannot fail to be appreciated by many of our readers. It consists of copious extracts from the Telegraphic Code book known as the "Unicode." Here we have a selection of phrases likely to be required in ordinary business transactions, with the code word appertaining to the phrase. Thus, if we want to send the message "Leaving on the 29th by steamship; do not forward any more letters, keep them until my return," it is only necessary to send the two words "Inhumo, Mellis,"—an important saving in foreign telegrams where so much a word is charged. The information in the diaries is of a useful description and is generally up to date. In one of the diaries, however, the list of Her Majesty's Ministers is omitted "in consequence of the General Election taking place while going to press,"—a reason we should scarcely have expected from a firm like Messrs. Cassell's.

The American Philosophical Society, held at Philadelphia for the promotion of useful knowledge, has the honour to announce that it will celebrate the 150th Anniversary of its foundation by a series of reunions at the Hall of the Society during the week beginning Monday, May 22, 1893, terminating on Friday, May 26, 1893, at which papers may be offered by title by such members as may be present. The Society invites the participation of scientific men on this memorable occasion.—*Committee*: J. SERGEANT PRICE, RICHARD VAUX, DANIEL G. BRINTON, WILLIAM V. KEATING, FREDERICK FRALEY (*ex-officio*), HENRY PHILLIPS, JUN. (*Chairman*).

MEETINGS FOR THE WEEK.

- MONDAY, 12th.—Society of Arts, 8. (Cantor Lectures). "The Generation of Light from Coal-Gas," by Prof. Vivian B. Lewes.
Medical, 8.30.
TUESDAY, 13th.—Institute of Civil Engineers, 8.
Chemical, 8. (Extra Meeting on the Anniversary of the death of Stas). "Jean Servais Stas, and the Measurement of the Relative Masses of the Atoms of the Chemical Elements," by Prof. J. W. Mallet, F.R.S.
Royal Medical and Chirurgical, 8.30.
Photographic, 8.
WEDNESDAY, 14th.—Society of Arts, 8. "The Utilisation of Niagara," by Prof. George Forbes, F.R.S.
Pharmaceutical, 8.
THURSDAY, 15th.—Royal, 4.30.
Chemical, 8. Ballot for the Election of Fellows.
"The Identity of Caffeine and Theine," by W. R. Dunstan and W. F. J. Shephard.
"Studies on Isomeric Change, 1:2:3-Ortho-xylene Sulphonic Acid, and Phenetolsulphonic Acid," by Dr. Moody.
FRIDAY, 16th.—Quekett Club, 8.

TO CORRESPONDENTS.

G. W. Blythe.—(1) Consult any elementary text-book on chemistry. (2) It cannot be bought. (3) Anhydrous ammonia is kept and sold under pressure in strong steel cylinders.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1725.

THE LUMINOSITY OF COAL-GAS FLAMES, PARTIALLY DUE TO THE OCCLUSION OF GASES BY THE CARBON PARTICLES.

By Dr. JAMES LEICESTER,

Lecturer on Chemistry and Metallurgy, Merchant Venturers'
Technical School, Bristol.

DAVY in 1818 accounted for the luminosity of flame as follows:—"The luminosity of flame is due to the decomposition of part of the gas towards the interior of the flame where the air is in smallest quantity, and the deposition of solid charcoal, which, first by its ignition and then by its combustion, increases in a high degree the intensity of the light."

Professor Smithells, in his paper on "The Structure and Chemistry of Flames" says:—"Air charged with benzene vapour yields a flame in which, after the two non-luminous cones have been separated and the supply of benzene vapour increased, a luminous tip appears in the inner cone, and on further increasing the benzene this tip extends as a vertical streak of separated carbon. It is luminous for some distance above the inner cone, then cools down, and only becomes incandescent again on passing through the tip of the upper cone. The carbon which is in the solid state must either undergo the usual glowing combustion, or escape from the flame unburned. As it does not do the latter to any appreciable extent it must burn, and the cessation of its combustion as a solid marks the limit of the yellow or luminous region of the flame."

Again, the higher we go in the flame the greater proportionally is the amount of separated carbon, for we have not only the heat of laterally outlying combustion to effect decomposition, but also that of the lower parts of the flame; the lower part of a luminous flame is accordingly cooler, and contains less separated carbon than the upper.

Professor Stokes has shown the separation of carbon, or carbon associated with hydrogen in flames, by its polarising effect on light.

Professor Vivian B. Lewes lays great importance upon the acetylene formed; he says:—"The luminous zone, in which the temperature ranges from 1100° to a little over 1300°: here the acetylene formed in the inner zone becomes decomposed by heat with liberation of carbon, which at the moment of separation is heated to incandescence by its own combustion and by the combustion of carbon monoxide and hydrogen, and gives luminosity to the flame. He has shown that oxidation, dilution, and cooling all help to bring about the destruction of luminosity in a Bunsen flame. In other words, the liberation of free carbon is reduced, and therefore the luminosity is diminished.

The various reasons here given refer entirely to the carbon particles being burnt or raised to incandescence by the heat of combustion of other constituents. It has occurred to me that possibly a portion of the luminosity might be due to the nascent carbon particles having the power of occluding certain of the gases, and thus being raised by the heat of condensation to incandescence.

As the further study of flames ought to be left to Prof. Smithells, I simply lay the suggestion before those chemists who are interested in the subject, and have communicated with him.

THE ANALYSIS OF FERROCHROME, FERRO- ALUMINIUM, FERROTUNGSTEN, FERROSILICON, AND FERROTITANIUM.*

By A. ZIEGLER.

THE author has published further communications recommending a mixture of caustic alkali and an alkaline nitrate for opening up the above iron alloys. They may be completely and quickly decomposed by fusion with a mixture composed of 6 grms. of chemically pure sodium or potassium hydroxide, and 3 grms. chemically pure sodium or potassium nitrate. 0.5 grm. of the alloy is used, pulverised, and sifted.

The process must be effected in a silver crucible, carefully observing the precautions given, so that the crucible may not be too much attacked, and a contamination of the melt with silver may be avoided as far as possible.

Ziegler uses a silver crucible holding about 50 c.c., and weighing from 45 to 46 grms. It must be heated with a reducing (smoky) flame, for which purpose the two air-holes of a Bunsen burner provided with a chimney are pasted over with paper, and very little air is admitted into the burner space by perforating the paper. During melting the crucible must be kept sooty.

For the analysis of ferrochrome $\frac{1}{2}$ grm. of the sifted sample is placed in the silver crucible and 6 grms. of chemically pure sodium hydroxide and 3 grms. of chemically pure sodium nitrate are added. The crucible is allowed to become sooty, and is heated with a rather small reducing flame, which is slowly increased. In about half an hour the process is complete if properly managed. When the contents of the crucible are cold (having been allowed to spread over the interior of the crucible shortly before congealing), it is placed in a porcelain capsule and filled up entirely with water. The solution may be expedited by stirring with a platinum rod.

When the salts are dissolved the contents are poured out, the crucible is wiped out and rinsed with water. The total liquid with the residue of ferric oxide is put into a beaker and is saturated with carbonic acid for half an hour. The entire mass is then evaporated to dryness in a porcelain capsule on the water-bath, dissolved in water and filtered. It is washed out with water containing a little sodium carbonate.

If these instructions are followed we obtain an almost complete separation of the silver from the other constituents of the alloy. The slight usually reddish deposit within the crucible seems to contain a little silver chromate, which is easily decomposed by means of dilute hydrochloric acid. The hydrochloric solution is added to the main bulk of the chrome solution, or these minimum portions of chrome are determined separately. The chromate solution is now concentrated to a known volume, the silica is separated in an aliquot portion by evaporating to dryness with hydrochloric acid, and in the filtrate the chrome is twice precipitated with ammonia. The portion of the melt insoluble in water contains all the iron, manganese, the chief part of the silica, &c. It is dissolved on the filter in hot dilute hydrochloric acid (1:3), the funnel being covered and washed in hydrochloric acid at 1 per cent. Here it generally appears if the opening up was complete. The hydrochloric solution is also evaporated to dryness, taken up with dilute hydrochloric acid and water, and filtered. Iron and manganese may be determined in the ordinary manner. The iron precipitate may be tested for chrome by means of the soda and nitre flux. The silica eliminated during the analysis is to be expelled by means of hydrofluoric acid, and any considerable residue is to be tested for chrome or manganese.

Silicon is most simply determined by opening up $\frac{1}{2}$ grm. of the substance with sodium bisulphate at a moderate

* From the *Zeit. Anal. Chem.*

heat, as at very high temperatures basic sparingly soluble sulphates are formed.

Rud. Namias, who uses bisulphate for opening up ferrochrome, adds, when the opening up is completed, a little more bisulphate, which, however, is unnecessary unless too strong a heat has been applied. If the process has been properly conducted the melt dissolves as good as completely (except the silica) in hot water acidulated with sulphuric acid on a longer or shorter digestion; an addition of hydrochloric acid, as Namias proposes, being unnecessary. The silica thus obtained is never chemically pure, and must for the sake of accuracy be evaporated down with hydrofluoric acid. The filtrate from the determination of silica may be used for titrating the manganese.

For determining the phosphorus Ziegler takes 2 grms. of the sample, which he opens up with 9 grms. soda salt-petre and 18 grms. potassium hydroxide. The melt is taken up with nitric acid and a little hydrochloric acid converted into a nitric solution by repeated evaporation with concentrated nitric acid, neutralised with ammonia, and the phosphorus determined as usual. The sulphur can also be determined with the same melt.

The weighed chromic oxide, if tested with a saltpetre soda melt is almost always free from iron and manganese. Any trace of silicon in the chromic oxide, except that due to the filters, can be detected by fusion with sodium bisulphate, since the chromium oxide is thus completely converted into soluble sulphate.

Ziegler points out that according to an earlier process salts of chromic oxide in a sulphuric solution can be converted into chromates by permanganate, and then determined volumetrically with ferroammonium sulphate. According to the author this process, if slightly modified, yields good results.

The sulphuric solution of ferrochrome obtained by opening it up with sodium bisulphate can be advantageously oxidised with permanganate. The manganese hydroxide is free from chrome, and the precipitate of iron and manganese obtained with sodium carbonate contains only minimum quantities of chrome.

(To be continued.)

VOLUMETRIC DETERMINATION OF SULPHURIC ACID BY THE CHROMATE METHOD.

By K. FARNSTEINER.

THE author heats the solution, slightly acidified with hydrochloric acid, almost to ebullition, and precipitates it with a measured excess of a solution of barium chloride of known strength. It is heated for some time longer, ammonia free from carbonic acid is added until the reaction is faintly alkaline, and the excess of barium chloride is then precipitated by means of a measured volume of potassium chromate of known power of reaction. When cold, the liquid (which now contains only a slight excess of potassium chromate), is transferred along with the precipitate into a suitable measuring flask, which is then filled up to the mark, well shaken up, and after the precipitate has subsided half the liquid is filtered off. It is then mixed with potassium iodide and hydrochloric acid, either in a beaker or in a wide-necked flask capable of being closed with a glass stopper. After some minutes the eliminated iodine is determined with a solution of sodium thiosulphate.

For the calculation the strength of the solution of barium chloride must be exactly known, as also the relation of the solution of chromate on the one hand to the solution of barium chloride, and on the other to the solution of sodium thiosulphate.

This method, however, does not give useful results for

large quantities of sulphuric acid, as both the barium sulphate and the barium chromate carry down potassium chromate. For the determination of small quantities of sulphuric acid (0.02 to 0.04 gm. SO_3), the method, according to the author, may be recommended, especially if ammonium chromate is used instead of potassium chromate. The method is suitable for the determination of sulphuric acid in soda, in common salt, potash, and potassium chloride, as also for ordinary water. Of this from 100 to 200 c.c. are heated with a little dilute hydrochloric acid to decompose the carbonates, and the sulphuric acid is precipitated with barium chloride. The liquid is then made very slightly alkaline with ammonia free from CO_2 , the solution of chromate is added, proceeding further as above.—*Zeit. Anal. Chem. und Chem. Zeitung.*

A PROCESS FOR THE QUANTITATIVE SEPARATION OF SILVER AND LEAD.

By R. BENEDICT and L. GAUS.

THE authors found their process on the different behaviour of silver and lead iodides with dilute nitric acid.

The solution containing silver nitrate and lead nitrate—in all about 0.5 gm. of metal—is diluted with cold water in a capacious glass capsule to from 200–300 c.c., and solution of potassium iodide more than sufficient for the complete precipitation of the silver, but not excessive in quantity, is allowed to flow in. If 0.5 gm. of metal is used, 10 c.c. of a 10 per cent solution of potassium iodide will be sufficient in any case. We then add 10 c.c. of nitric acid free from chlorine, previously diluted with from 10–20 c.c. of water. The capsule is then covered with a watch-glass and heated on the water-bath, when the yellow colour of the precipitate chiefly passes at first into orange-red.

As soon as the liquid has become hot, the lead iodide dissolves, the liquid becomes dark brown, and vapours of iodine are given off. The watch-glass is then removed and rinsed into the capsule, boiling water is added, and the capsule is left on the water-bath, adding water from time to time to compensate for the loss by evaporation until the liquid has become colourless or pale yellow, when the iodine is expelled. The silver iodide is then weighed. The authors collect it in a small glass tube filled with glass wool, dried at 110° , and weighed. Wash it first with hot water containing nitric acid, and then with a few c.c. of hot water, dry at 110° and weigh.

The presence of other metals of the same group, with the exception of mercury, does not interfere. Cuprous iodide, bismuth, and cadmium iodide behave with nitric acid like lead iodide; on the other hand, mercurous iodide is converted into red iodide, which is not further attacked.

The authors publish very favourable results. In the examination of alloys of lead and silver they proceed in the same manner. They dissolve in nitric acid, dilute, precipitate with potassium iodide, and heat on the water-bath.

For determining silver in impure leads, from 10–50 grms. of the same, according to the proportion of silver, is dissolved in dilute nitric acid containing tartaric acid. To 10 grms. of the sample they use 10 c.c. nitric acid free from chlorine, and an equal quantity of a saturated solution of tartaric acid. The presence of the latter effects much more rapid and complete solution. The solution is heated until the oxidation is completed, diluted with boiling water, filtered into a glass capsule, diluted to from 300–500 c.c., allowed to cool, 10 c.c. of a 10 per cent solution of potassium iodide are added, and it is heated on the water-bath.

The excess of the nitric acid added for solution is

generally sufficient for oxidising the lead iodide; if the development of iodine vapours and the brown colour do not appear, a little more dilute nitric acid must be added.

The proportion of silver in galena may be determined in the same manner. It is oxidised with nitric acid with the addition of tartaric acid. It is most convenient to use equal volumes of nitric acid, solution of tartaric acid, and water. After the oxidation is completed, the liquid diluted with hot water, filtered, and well washed with boiling water, the filtrate is allowed to cool. The process is then completed as above.—*Zeit. Anal. Chemie und Chem. Zeitung.*

PHOSPHORIC ACID IN BERYL.

By FRANKLIN C. ROBINSON.

SEVERAL years ago (spring of 1883) Prof. J. Torrey, jun., now of the Harvard Laboratory, then a student in Bowdoin, found a mineral in the neighbouring town of Yarmouth which was of such peculiar appearance that I suggested that an analysis be made. Its appearance suggested a beryl; that is, it was of the well-known beryl form, but had hardly the suggestion of green colour and the crystallisation was rather indistinct. His analysis gave silica lower and alumina higher than they should be in beryl, and in addition phosphoric acid and alkalis were discovered to the amount of several per cent. Our notes, made at the time, show that while sodium and potassium were the chief alkalis in amount, undoubted traces of lithium and caesium were also present.

Our decision then was that the mineral was probably not a beryl, and it was laid aside for future work. Since then, as is well-known, other observers have proved the general presence of alkalis in beryl, and I have only awaited a favourable opportunity to re-examine the specimen and see if, after all, our first impression as to its being a beryl may not have been correct. My assistant, Mr. C. H. Cutts, has now made such re-examination with the following results:—

Colour, grey to white, with mere trace of green.	
Hardness, 7. Specific gravity, 2.627. Loss on drying at 100° C., 0.33 per cent.	
Loss on ignition	1.53 per cent.
Silica	64.70 "
Alumina	17.76 "
Beryllium oxide	12.18 "
Phosphoric acid	2.76 "
Alkalis (Na ₂ O, K ₂ O, Li ₂ O, Cs ₂ O)	1.10 "

100.03

Regarding the phosphoric acid and alkalis as replacing a part of the beryllium, we have the numbers 1, 2, 6, 12, for water, alumina, beryllium oxide, silica, respectively, showing that the mineral is really a beryl. The former low result in silica was not obtained owing to greater care in selecting a pure specimen for analysis.

The presence of phosphoric acid in this led me to have it tested for in other specimens of beryl, with the result that its presence has been detected in nearly every case; but in no other specimen has so large a percentage been found. I am unaware that any notice of the fact that phosphoric acid is frequently present in beryls has before been published.—*Journal of Analytical and Applied Chemistry*, vi., No. 9.

The Functions of Hydurilic Acid. Preparation of Potassium Hydurilates.—C. Matignon.—Hydurilic acid is tribasic. It possesses three different acid functions. The first comparable to the strongest acids of organic chemistry; the second of the same order as that of the normal carboxylic acids, and the third inferior to the feeble function of phosphoric acid.—*C. R.*, cxv., No. 22.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 1st, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

DRS. WILLIAM J. MCKERROW, John Shields, James Walker, and W. P. Wynne were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Edwin Brockbank, The Croft, Kirksanton, *viâ* Carnforth; Edward Brooke, West Court, Chalk, Gravesend, Kent; Charles Dreyfus, Ph.D., Clayton Aniline Co., Clayton, Manchester; James Elias, Briton Ferry, Glamorganshire; Alexander Stanley Elmore, Twait Gate, Leeds; George Neville Huntly, 56, Sheen Road, Richmond, Surrey; Charles M. Luxmore, B.Sc., 529, Battersea Park Road; Robert Henry Owen, Pas-y-coed, Troedyrhiw, near Merthyr Tidfil; John William Towers, Brantwood, Allerton, near Liverpool; William Ernest Wheeler, Cumberland House, Meynell Road, South Hackney.

Of the following papers those marked * were read:—

*70. "The Isolation of Two Predicted Hydrates of Nitric Acid." By S. U. PICKERING.

In the case of nitric acid the curves plotted from both Berthelot's and Thomsen's heat of dissolution values were found to exhibit a well-marked "break" at the composition of the trihydrate; Kolb's density values afforded a similar indication, and also exhibited a "break" at the monohydrate; on making a series of freezing-point determinations, both these hydrates, but no others, were isolated in the crystalline condition. The melting-point of the trihydrate is -18.2° , and that of the monohydrate -36.8° . In the case of each the melting-point is lowered by the addition of either acid or water. These results are regarded by the author as an important confirmation of the views expressed by him in previous papers.

*71. "Anhydrous Oxalic Acid." By W. W. FISHER M.A.

Although the crystallised dihydrated acid is a familiar substance, anhydrous oxalic acid is but little known, except as a roughly dried mass, probably because it so readily attracts moisture. E. Reichert has shown that it is obtained from the hydrate by treatment with concentrated sulphuric acid (*Jena Zeit.*, 1864, vol. i., p. 244), but he states that the excess crystallising from a heated mixture of the two substances is a hydrate; this, however, appears to be an error. A. Villiers, in 1880 (*Compt. Rend.*, xc., 821), published a note on the crystals obtained by this method, and pointed out that they were of greater relative density than sulphuric acid. The crystalline form of the anhydrous acid has been described and figured by Löschmidt (*Wien. Akad. Ber.*, 1865), but owing to the readiness with which the crystals change in air, the determinations were but approximate; they are prismatic octahedra, resembling elongated crystals of alum.

The best method of producing the crystals is to allow ordinary hydrated oxalic acid to remain in contact with concentrated sulphuric acid for a few months; if the two substances are sealed up together in a glass tube, beautiful specimens may be obtained. Oxalic acid, whether hydrated or not, is sparingly soluble in sulphuric acid, about 3 per cent being taken up by the cold liquid. The anhydrous acid dissolves with a slight fall of temperature, while a rise of temperature is noticed when the hydrated crystals dissolve. Dissolution takes place readily on warming, and part of the dissolved acid separates in the anhydrous state on cooling the solution, a supersaturated liquid being obtained from which the excess is slowly deposited.

The relative density of the crystals, determined in dry petroleum, was found to be 1.878 compared with water at 4°, while the density of the hydrated acid similarly determined was found to be 1.608 (Bödeker, *Fahresb.*, 1860, 17, gives $d=2.0$). This difference affords a ready means of distinguishing the hydrated crystals, as when placed in concentrated sulphuric acid they at first float, but losing their transparency and turning white as they become dehydrated, they increase in density and finally sink to the bottom.

The limit of concentration at which crystallised oxalic acid in contact with sulphuric acid retains its water is between 60 and 70 per cent at ordinary temperatures, as the hydrated form is unchanged in the weaker acid and the anhydrous crystals are permanent in the 70 per cent sulphuric acid.

Hydrated oxalic acid behaves in a similar manner towards nitric acid, as it may be re-crystallised from that containing about 70 per cent of real acid ($d=1.2$) without losing its water, while in a highly-concentrated acid ($d=1.50$) it is dehydrated.

The crystals deposited from nitric acid are usually less brilliant in appearance and smaller than those formed in sulphuric acid.

Commonly, oxalic acid is dried by the rough method of heating in an open dish, when a considerable part of the water is expelled, but much loss takes place by volatilisation, and unless the acid be actually sublimed the drying is still imperfect. It can, however, be easily and completely dried in a vacuum by means of the arrangement described by McLeod (*C. S. Trans.*, 1883, 384) or in an ordinary retort; for this purpose the retort containing the acid is attached to a receiver containing strong sulphuric acid, exhausted by a water vacuum pump, and heated at 60° on a water-bath; in a few hours the theoretical quantity of water is expelled from the crystals.

A specimen dried in this manner, which had been transferred to a tube, then sublimed in a vacuum by a steam heat and sealed up in the year 1890, appeared in the ordinary form of the sublimed acid as a mass of needles, but after a few months, by slow re-sublimation at ordinary temperatures, the interior of the tube became coated with brilliant crystals resembling those deposited from sulphuric acid.

The volatility of hydrated oxalic acid was observed by Faraday (*Journal Royal Institution*, 1830), who found that when kept in an open tube for four years within a stoppered bottle containing calcium chloride, some oxalic acid passed over into the calcium solution, and new crystals were visible on the surface of the old ones. The hydrated acid does not appear to sublime as readily as the anhydrous form, specimens enclosed in vacuum tubes showing, after several months, hardly any signs of volatility.

The stability of oxalic acid is evidenced by the fact that it can be readily sublimed in a vacuum at temperatures up to 150; and that, even if heated on the water-bath in concentrated sulphuric acid, a portion will sublime from the liquid undecomposed.

Anhydrous oxalic acid will dissolve in warm ethylic oxalate or glacial acetic acid, but does not crystallise well from either solvent, only a powdery product being obtained.

*72. "The Production of Orcinol and other Condensation Products from Dehydracetic 'Acid.'" By N. COLLIE, Ph.D., and W. S. MYERS, B.Sc.

Oppenheim and Precht have stated (*Ber.*, 1876, 324) that orcinol is formed when dehydracetic "acid" is hydrolysed by means of barium hydrate, but they obtained only a very small quantity, and based their conclusion on qualitative evidence; their observation is now corroborated by the authors, who have obtained orcinol, not only from dehydracetic "acid" and dimethylpyrone by the action of barium hydrate, but also by boiling a mixture of syrupy caustic soda and dehydracetic "acid"; in the

latter case a true (carboxylic) acid is first produced, which loses carbon dioxide, leaving orcinol.

Among the products obtained on submitting diacetyl-acetone to the action of barium hydrate, the authors have discovered a substance crystallising in bright yellow needles melting at 180—181°, which is probably a naphthalene derivative, its formation involving the change expressed in the equation $2C_7H_{10}O_3 = C_{14}H_{14}O_3 + 3H_2O$. Mention is also made of a substance exhibiting a magnificent blue fluorescence formed in the preparation of diacetylacetone from dimethylpyrone by treatment with baryta water.

An amidodehydracetic "acid" is described, which is formed by the interaction of solid dehydracetic "acid" and the strongest ammonia solution; it crystallises in long silky needles, m.p. 192—196°, and is readily re-converted into dehydracetic "acid" by alkaline or acid hydrolysis.

*73. "Observations on the Origin of Colour and on Fluorescence." By W. N. HARTLEY, F.R.S.

Adverting to the arguments used by Armstrong in the *Proc. Chem. Soc.*, 1888, iv., 27, the author defines colour and the cause of colour, the nature of visible and invisible colour, and the limits of visibility in the spectrum from a physical standpoint. It is contended that it cannot be stated in general terms that colour is due to special modes of atomic arrangement, but that the statement may be applied in a restricted sense to certain carbon compounds, especially to those included in the class to which organic dye-stuffs belong; and it is pointed out that all open chain hydrocarbons exert a continuous absorption, the extent of which depends on the number of carbon atoms in the molecule.

Attention having been drawn by Armstrong to the condition of strain and of instability existing in many coloured substances, it is pointed out that this is owing to their being all endothermic compounds; that ethylene, acetylene, and benzene are endothermic, but that derivatives of the last-named only are coloured; and finally that all organic colouring matters are endothermic compounds.

This is considered to be the physical cause of that which Armstrong has not defined, but which he terms "reactivity" or "high potential."

It is next shown that anthracene is not colourless, but has a true greenish yellow colour in addition to its fluorescence.

The results of a number of experiments on fluorescence are then given in detail, and from these the following conclusions are drawn:—

1. Quinine dissolved in alcohol exhibits a beautiful bright violet fluorescence.
2. Chlorhydric acid is not fluorescent.
3. Quinine hydrochloride is very feebly fluorescent, but without distinct colour.
4. Chloroform is feebly fluorescent, but without distinct colour.
5. Both chlorhydric acid and chloroform can extinguish those rays which are the cause of the fluorescence in quinine.
6. Some alkaloids may be recognised by the degree and colour of the fluorescence they exhibit.
7. Normal alcohols of the ethylic series are fluorescent; so, also, are the fatty acids.
8. Glycerol has a violet fluorescence.
9. Benzene has a pale blue fluorescence, azobenzene a greenish blue.
10. Rock crystal has a pale bluish-violet fluorescence, flint glass a strong blue, and crown glass a very brilliant and beautiful blue fluorescence.
11. Substances which are not fluorescent in strong solutions may become so on dilution, particularly if they exert a very powerful absorption of the ultra-violet or visible spectrum.

The colour and fluorescence of anthracene are ex-

plained. Finally, the case of ortho- and para-nitrophenol and of meta- and para-nitraniline are discussed, and it is contended that the formulæ of ortho nitrophenol and metanitriline should not at present undergo modification.

*74. "The Origin of Colour. (V.) Coloured Hydrocarbons and Fluorescence: a Reply to Prof. Hartley's Observations on the Origin of Colour and of Fluorescence." By HENRY E. ARMSTRONG.

A perusal of my friend's objections leaves me under the impression that he scarcely apprehends my views on the origin of colour, and that he does not fully comprehend my aim; but this is not surprising, my arguments having hitherto been published in the briefest and most condensed form, as I have always felt that, in dealing with so difficult and extensive a subject, it was necessary to proceed slowly, and to read, mark, learn, and give much time for inward digestion and further experimental study before venturing to discuss in detail the manifold issues involved. My critic having clearly accentuated many of the points which demand consideration, I am in consequence much indebted to him; moreover, the fact that he has paid special attention to the study of ultra-violet absorption-spectra lends great weight to his statements, which serve also to indicate the departure from current views involved in the adoption of the hypothesis of which I am an advocate. I have never left out of account the fact that, in a physical sense, all substances are coloured—all substances possessing the power of absorbing the light waves, either generally or selectively, in some part either of the visible or invisible spectrum. My contention has been simply that, confining our attention to visibly coloured organic substances to substances coloured in the ordinary conventional sense, it is a most remarkable fact that in those cases in which the "constitution" of the coloured substance is fairly well established, coloured substances are all of one type, and from this base I have started on the inquiry whether all coloured organic compounds are not similar in type.

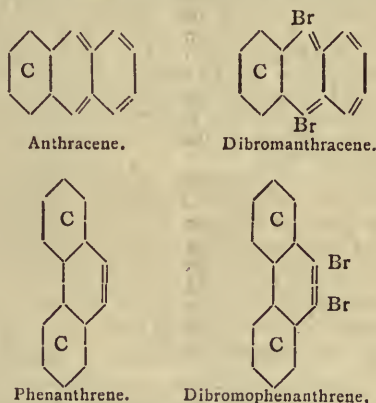
According to Hartley, "in order to study the origin of colour, we must first consider the case of colour in those molecules which are of the simplest possible constitution, such as, for instance, the molecules of chlorine, oxygen, ozone, and water." Undoubtedly this would be the case if we knew their "constitution"; but we do not, our knowledge being confined to the fact that their molecules consist of a certain number of atoms—which is insufficient. He also asserts that "the colour or effect on light caused by molecules of oxygen, ozone, and water, is in no way different from that caused by molecules of aniline blue." This may or may not be a correct interpretation of the facts; apparently the molecules of both oxygen and ozone are intrinsically coloured, but is the water molecule? It is an important question for experimental investigation whether water in a perfectly gaseous state would be blue when viewed in a column of sufficient thickness; its colour may originate in the poly-molecules which presumably are contained in the liquid.

My critic furthermore states that "all organic colouring matters are endothermic compounds." This may well be the case, but the converse does not hold, as he himself recognises, and the conclusion helps us but little; such a phrase, in fact, serves but to obscure the issue by merging the less in the greater.

A most important section in the paper under notice is that relating to fluorescence, describing a series of observations which lead their author to conclude that many substances are fluorescent which hitherto have not been considered to be so, e.g., alcohol and its homologues, &c. There can be no question as to the accuracy of these observations, but until many of the substances have been further studied, and every possible precaution has been taken to obtain them *pure*, I must, with all deference, decline to accept all the results as final. In the case of naphthalene derivatives, especially the naphthyl-amine and naphthol-sulphonic acids, with which I am somewhat

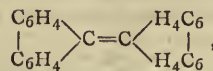
familiar, intensely fluorescent solutions are the rule—yet I very much doubt their being fluorescent, having noticed time after time, that the more nearly pure the substance becomes, the less fluorescent it is. It is easy also to account for the presence of fluorescent impurities in these cases on the assumption that during the heating with sulphuric acid oxidation takes place, and that the resulting phthalic acid, or nearly allied compound, condenses, forming a fluorescein; a strong argument in favour of this explanation is afforded by the fact that the disulphonic acids which are formed with the aid of fuming acid at somewhat elevated temperatures, and are very soluble, and therefore difficult to purify, are far more strongly fluorescent than the monosulphonic acids, which are difficultly soluble and comparatively easily purified.

In considering the "origin of fluorescence" and in regarding it as the "beginning of colour," I am, undoubtedly, entering into a highly speculative region; yet the facts are very striking. A single example will suffice. Anthracene is intensely fluorescent, and it may be represented by a quinonoid formula; the isomeric hydrocarbon, phenanthrene, however, which cannot be so represented, is colourless and non-fluorescent, according to present knowledge. Hartley's discovery that anthracene has a visible slight greenish yellow colour is to me one of extreme interest, and I cannot refrain from referring to it as a very strong confirmation of my hypothesis. Furthermore, while an intense yellow colour is produced by "weighting" what may be termed, for convenience, the "quinonoid radicles" of anthracene by introducing chlorine or bromine in place of the central hydrogen atoms, no such effect follows the introduction in a similar manner of bromine into phenanthrene, dibromophenanthrene being colourless like the hydrocarbon. And yet anthraquinone and phenanthraquinone are both coloured, the latter being deep orange and the former yellow.



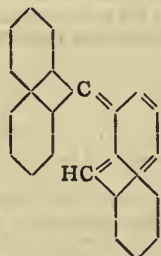
Much more evidence of this character might be added, but I have said sufficient to show why Hartley's arguments have not shaken my conviction that we may eventually be led to regard fluorescence as a feeble manifestation of that which we ordinarily describe as colour.

While speaking of anthracene as a coloured hydrocarbon, reference may be made to other coloured hydrocarbons, of which we now know several, viz., carotin, and the red hydrocarbon, $C_{26}H_{16}$, obtained by van Dorp and de la Harpe by passing fluorene over heated lead oxide, which has recently been investigated by Graebe (*Ber.*, 1892, 3146). We know nothing of carotin at present. Graebe represents the hydrocarbon from fluorene by the formula—

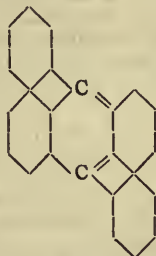


and therefore terms it dibiphenylenethene; I venture to suggest that it would be more appropriately named *Ery-*

throphene, a term which does not commit us to any definite view as to its constitution. I have no hesitation in asserting that a hydrocarbon represented by the formula proposed by Graebe would be colourless, and I would suggest the formula given below as more probable; at the same time it may be pointed out that the *yellow* hydrocarbon $C_{26}H_{14}$ (*xanthophene*), which van Dorp and de la Harpe obtained together with "erythrophene," may be a diphenylenated anthracene.



Erythrophene.



Xanthophene.

Both hydrocarbons are represented by quinonoid formulæ and the "quinonoid radicles" are heavily "weighted"; hence they are somewhat intensely coloured.

As to the nitrophenols, I have not called in question the constitution of the ortho-compound simply because it has a yellow colour; I have also pointed out that it differs in many other respects in a marked manner from its isomerides. Hartley's remarks appear to me in no way to affect my argument. With reference to the nitro-compounds, he states that "a very little shifting of the region of absorption to rays a little more or a little less refrangible, makes such substances colourless or coloured." No doubt this is so, but the question I would raise is whether the shifting necessary for the production of visible colour (and in a measure of fluorescence) is not conditioned by a special character of structure. In such a case as that of diorthonitrophenol, for example, which is yellow and affords intensely red metallic derivatives, yet yields colourless ethers, it is very difficult to avoid the conclusion that this is so; if we consider the propyl and potassium derivatives, the change from colour to colourlessness, or *vice versa*, cannot be conditioned by a change in "weight" of the radicles, as they are so nearly alike in this respect; Hartley, I imagine, would attribute the difference to the higher "energy" of the metallic radicle, but this latter idea is also, in a measure, included in my suggestion that colour in such a case is developed as a consequence of an isodynamic change, and it must not be forgotten that the evidence of changes of this character occurring is rapidly increasing in volume, *e.g.*, Perkin's recent observations on the magnetic rotation of compounds supposed to contain acetyl.

Hartley's explanation of the non-fluorescence of quinine hydrochloride—that it is due to the absorption by the hydrogen chloride solution of the very rays which are the cause of the fluorescence in quinine—is both simple and satisfactory, and I have no hesitation in accepting it; but this in no way alters my conviction that the fluorescence of quinine itself is in all probability conditioned by peculiarity of structure.

Finally, I do not understand why "analogy" should lead us to expect hydrogen chloride to be coloured because chlorine is, or nitric acid to be coloured because NO_2 is; in such cases, we have, I think, at present no reason to expect analogous behaviour, nor indeed any information at our disposal from which conclusions can with justice be drawn.

In the discussion on a previous occasion (*Proc. Chem. Soc.*, 1892, 105), I said that it appeared probable to me that ultimately colour would be traced to that peculiar condition represented conventionally by a double bond, the

atoms being regarded as altogether subordinate. It is perhaps desirable that I should now more fully explain my views as to the manner in which the "quinonoid mechanism" conditions colour.

Briefly, I would suggest that in quinonoid compounds there are two "colour centres," corresponding to and expressed by the symbol $\subset$ in formulæ such as I have used in representing coloured substances. These centres, I imagine co-operate in producing colour through interaction of the light-waves which have traversed them. Substances in which there are no such co-operating centres may absorb generally or selectively in "ultra" and "infra" regions of the spectrum, but without exhibiting "visible colour." In this manner, it is possible, I think, to account for the appearance of colour in substances like diacetyl, $Me \cdot CO \cdot CO \cdot Me$, and dibenzoyl, $Ph \cdot CO \cdot CO \cdot Ph$, in which there are two contiguous CO groups—*i.e.*, which possess a pseudo-orthoquinonoid structure without being quinones.

The colour centres may be likened to elastic gratings, in order to represent the modifications induced by attaching different radicles; in order to account for variation in shade of colour, such elastic gratings may be pictured as undergoing "longitudinal" and "lateral" deformations, varying in extent and character according as the "weight" and character of the attached radicles is varied, and as capable, therefore, of differently affecting the incident rays. However incorrect, from a physical standpoint, this imagery may appear, I trust it will suffice to make my meaning clear.

It is not inconceivable that the distinction which I have sought to make between visible colour and physical colour is no arbitrary one, but is inherent in the human optic mechanism; that our perception of colour, in fact, is itself conditioned by, and exerted through, the agency of quinonoid matters. The discussion of the origin of colour from this point of view, appears, therefore, to be of importance to physiologists, as well as to chemists and physicists.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, December 9th, 1892.

Mr. WALTER BAILY, M.A., Vice-President, in the Chair.

Mr. H. E. RAWSON was elected a member of the Society.

The CHAIRMAN announced that an extra meeting would be held on January 13, 1893.

Prof. S. P. THOMPSON's communication on "Japanese Magic Mirrors" was postponed.

Mr. W. B. CROFT, M.A., read a paper on "The Spectra of Various Orders of Colours in Newton's Scale."

After referring to the definition of the order of colours by reference to the retardation wave lengths produced by different thicknesses of selenite between crossed polariser and analyser, the author went on to say that several books on optics implied that the number of bands in the spectra of these colours was the same as the order of the colour. On obtaining selenites of the first four orders of red from Messrs. Steeg and Reuter, he found that the first three orders gave one dark band each, and that of the fourth order three dark bands. Further experiments showed that the thicknesses of the selenites were in the proper proportions required to give the first four orders of red. The numbers of bands, the author explained, depended on the numerical possibilities of wave length within the visible spectrum; that is, whether a multiple of the wave length of one visible wave can be another multiple of a different wave. For example, taking the visible spectrum as extending from A (0.000760 to H (0.000394), and the wave length of the line E in the green as 0.000527 , it was shown that the first order of red

was due to extinction of green by a thickness of crystal proportional to 1×0.000527 , and would give one band in the green. For the second order, the thickness of crystal was proportional to 2×0.000527 , viz., 0.001054 , and this number was no other integral multiple of any other wave length between A and H; consequently there could only be one band. Similarly it was shown that the third order of red could only have one band or possibly produce a shortening of the spectrum. With the fourth order of red three bands were obtainable, for—

$$4 \times 0.000527 = 3 \times 0.000703 \text{ and } = 5 \times 0.000422.$$

Three bands were therefore possible near E, A, and G, respectively.

At the conclusion of his paper, Mr. CROFT directed attention to a very simple form of diffraction apparatus, by which most of the ordinary diffraction phenomena could be well seen, and which also served for spectrum observations.

Mr. H. MIERS pointed out that in Lewis Wright's "Practical Optics," a chart showing the bands corresponding to the first four orders of red was given. So far as he was aware, the subject was not fully discussed in the book.

In reply, Mr. CROFT said he had noticed Mr. Wright's chart, but believed that the text implied that the number of bands should be the same as the order of the colour. Tyndall made definite statements to that effect.

Dr. W. E. SUMPNER read a paper on "The Diffusion of Light."

The influence of diffusion in increasing the illumination of rooms and open spaces had not, in the author's opinion, been sufficiently appreciated. Being impressed with the great importance of the subject, he was led to make determinations of the coefficients of reflection, absorption, and transmission of diffusing surfaces. To give precision to terms sometimes vaguely used, several definitions were proposed. *Reflecting power* was defined as the ratio of the amount of light reflected from a surface to the total amount of light incident upon it; *illumination* of a surface, as the amount of incident light per unit of surface; *unit quantity* of light as the flux of radiation across unit area of a sphere of unit radius, at whose centre a unit light is placed; and *brightness* as the candle-power per unit area in the direction normal to the surface. Denoting these quantities by η , I , Q , and B respectively, and assuming the cosine law of diffusion (i.e., the candle-power in any direction is proportional to the cosine of the angle between the direction and the normal to the surface) it was shown that $\pi B = \eta I$, and that the average illumination (I') of the walls of a room is related to the illumination (I) due to the direct action of the lights as expressed by the formula—

$$I' = \frac{I}{1 - \eta}.$$

If the reflecting power of the walls, &c., be 50 per cent, $\eta = \frac{1}{2}$, and $I' = 2I$; whilst if $\eta = 0.8$ (a number approximately true for white surfaces), then $I' = 5I$. The illumination due to the walls may therefore be far more important than that due to the direct rays from the lights. When the surfaces consist of portions of different reflecting power, the average may be found from the equation—

$$\eta = \frac{\eta_1 A_1 + \eta_2 A_2 + \&c.}{A}$$

A being the total surface, and A_1 , A_2 , &c., the areas of surfaces whose reflecting powers are η_1 , η_2 , &c., respectively. This law is shown to be quite accurate for spherical enclosures.

In measuring reflecting power, the surface was attached to a large screen of black velvet placed perpendicular to a 3 metre photometer bench. Two lights were used, one a Methven 2-candle standard placed at the end of the bench remote from the reflecting surface, and the other, a glow lamp of about 20 candle-power, was attached to a

slider which also carried a Lummer-Brodhun photometer. The glow-lamp served to illuminate the reflecting surface, but the photometer was screened from its direct rays. The formulæ used in reducing the observations are worked out in the paper, and tables of results given.

Absorbing power was determined by measuring the candle-power of a glow lamp, first when uncovered, and then when surrounded by a cylinder of the substance under test. It was found to be of great importance to distinguish between apparent and real absorption; for reflection from the surfaces of the cylinders increases the internal illumination. The true absorption coefficient (α) is given by—

$$\alpha = (1 - \eta) \frac{k_0 - k_1}{k_0};$$

where η is the reflecting power, and k_1 and k_0 the candle-powers with and without the envelope of material under test.

In determining transmitting power, the Methven standard and photometer were placed on one side of the surface, and the glow lamp on the other. Difficulties were experienced from the fact that some materials, such as tracing-paper, transmit part of the light directly (like transparent substances) and another part by diffusion, according to the cosine law. Methods for discriminating between the different parts were therefore devised, both in the reflection and transmission experiments, and consistent results subsequently obtained. Tables and curves showing the close agreement of calculated and observed values are included in the paper. An abstract of some of the tables of numbers is given below.

Material.	Percentage reflecting power, η .	Percentage absorption, α .	Percentage transmission, τ .	$\eta + \alpha + \tau$.
Blotting paper ..	82	13.8	9.2	105.0
Cartridge paper..	80	12.2	11.2	103.2
Tracing cloth ..	35	15.0	54.4	104.4
Tracing paper ..	22	7.0	76.0	105.0
Ordinary mirror ..	82	—	—	—
Ordinary foolscap	50 to 70	—	—	—
Tissue paper (one thickness) ..	40	—	—	—
Tissue paper (two thicknesses) ..	55	—	—	—
Yellow wall paper	40	—	—	—
Blue paper.. ..	25	—	—	—
Dark brown paper	13	—	—	—
Yellow painted wall.. ..	20	—	—	—
Black cloth ..	12	—	—	—
Black velvet ..	0.4	—	—	—
Arc lamp globes—	—	Apparent	—	—
Light opal ..	—	15	—	—
Dense opal ..	—	39	—	—
Ground glass..	—	42	—	—

Theoretically, the sum of the reflecting, absorbing, and transmitting powers should be unity, but from the above Table it will be noticed that they exceed one-hundred per cent by amounts greater than can be accounted for by experimental error. This discrepancy the author thought might be attributed to the law of cosines not being exactly fulfilled.

Mr. A. P. TROTTER said he had been interested in the subject of diffusion for many years with a view to obviating the glare of arc lamps. Some experiments he made on reflecting power gave unsatisfactory results, owing, as he now saw, to his not taking the solid angles subtended by the reflecting surfaces into account. The reflecting power of substances was of great importance in the illumination of rooms; in one case, measured by Dr. Sumpner and himself, two-thirds of the total illumination was due to the walls. It would greatly simplify measurement of reflecting power if some substance could be adopted as a standard.

Referring to the cosine law, he said he had found it true, except when the angles of incidence approached 90° . In cases where considerable total reflection took place, the apparent brightness near the normal direction was greatly in excess of that in other directions. These points he illustrated by polar curves. He had also considered what should be the nature of a roughened or grooved surface to give the cosine law of diffusion. No simple geometrical form of corrugations, &c., seemed to fulfil the required conditions.

Dr. HOFFERT said the high numbers given for the reflecting powers of substances were very interesting. Most people had noticed the effect of laying a white tablecloth in an ordinary room. He had also observed that wall papers of the same pattern, but slightly different in colour, had very different effects in producing increased illumination, and wished to know if the influence of small differences in colour and texture on diffusing power had been investigated.

Mr. BLAKESLEY defended the cosine law and suggested that the summation of the powers exceeding unity might be due to the fact that the enclosure reflected heat as well as light, thus raising the temperature and increasing the efficiency of the radiant.

Mr. ADDENBROOKE said the importance of the subject was impressed on him when he passed through America three years ago and noticed the crude manner in which electric lighting was there carried out. If using good reflecting surfaces increased the illumination of a room 50 per cent, it was like reducing the cost of electricity from 8° to 4° per unit. He could hardly conceive any subject of more practical importance than the one before the meeting.

Dr. C. V. BURTON did not understand why the cosine law should be objected to, for it was possible that no surface was perfectly diffusive. The effect of reflection from walls, &c., say in illuminating a book, would not, he thought, be so great as would appear from the numbers given, for one usually read near a light, and the reflected light falling on the book was only a small part of the whole, on account of the greater distances of the walls.

Another MEMBER pointed out that in experiments such as those described, it was very important to screen the photometer and surfaces from all radiation other than that under test. He rather doubted whether any surface reflected as well as mirrors. White surfaces might appear to do so, but this was probably because the eye would over-estimate it, owing to the superiority of white in aiding distinct vision.

Dr. SUMPNER, in reply, said he had, as stated in the paper, used white blotting-paper as a standard of reflecting power, and found it very convenient. His most careful measurements had been made on whitish surfaces, and not on coloured ones. Where one colour, say red, preponderates in a room, the average light would be much redder than that emitted by the source owing to the other colours being absorbed.

In considering illumination as related to distinct vision, it was necessary to take account of the eye itself, for the pupil contracted in strong lights and opened in feeble ones. This subject he hoped to treat fully in a subsequent paper.

Action of the Chlorides of Bibasic Acids upon Sodium Cyanacetic Ether.—Th. Müller.—In the action of succinyl chloride upon sodium cyanacetic ether there are formed two products, which may be separated by means of sodium carbonate, succinocyanacetic ether, insoluble in this reagent, and succinodicyanacetic ether, which dissolves in it with escape of carbonic acid. The author does not decide on the constitution of these two ethers, though the former has probably a dissymmetric constitution. The other is doubtless a symmetric compound.—*Comptes Rendus*, cxv., No. 22.

NOTICES OF BOOKS.

Berzelius and Liebig. Their Correspondence from 1831 to 1845; with Explanatory Additions from the simultaneous Correspondence of Liebig and Wöhler, as well as Scientific References. ("Berzelius und Leibig. Ihre Briefe von 1831 bis 1845; mit erläuternden Einschaltungen aus gleichzeitigen Briefen von Liebig und Wöhler so wie, wissenschaftlichen Nachweisen herausgegeben, mit Unterstützung der kgl. Bayer Akademie der Wissenschaften von JUSTUS CARRIÈRE.")

Edited by JUSTUS CARRIÈRE, with the Assistance of the Bavarian Academy of Sciences. Munich and Leipzig: J. F. Lehmann.

THIS collection of letters is a most precious document for all who feel an interest in the history of chemistry during the second quarter of the present century, and in the life and character of some of its most distinguished representatives. Berzelius and Liebig appear here doubtless as genuine men of science, actuated by a pure disinterested love for truth, but at the same time as somewhat prone to take offence and sufficiently severe towards opponents. Wöhler, on the contrary, equally devoted to science, displays here his genial, kindly disposition in seeking to smooth over offences and to explain misunderstandings. Not a few of their contemporary *savants*, French and English, as well as German, experience warm denunciations. Whether Berzelius or Liebig is the more outspoken on such occasions would be hard to decide. Liebig defends his old master, Gay-Lussac, against the mistaken dislike expressed by Berzelius; but he admits that a certain mental indolence restrains the French, to their disgrace, from making themselves acquainted with foreign research. Gay-Lussac, he adds, fears that this tendency will lead to the extinction of all scientific feeling in France.

Dumas is humorously spoken of as a Jesuit, named Ignatius, and accused of "impudent falsehoods." The scientific men, alike of Paris and Berlin, are pronounced "jealous *savants* who never enjoy science, but merely their momentary reputation."

We find a notice of the controversy touching the discovery of vanadium. Humboldt claimed the honour for Del Rio, whilst Berzelius insists upon the rights of Sefström. Possibly the position of Del Rio would have been stronger if he had not yielded to the influence of Descotils, who insisted that it must be chrome.

Under date May, 1831, Liebig characterises Giessen as a place where the dreariest pedantry has set up its throne, and where the natural sciences were taught only out of Greek authors, or from the writings of Wilbrand. So that in spite of the influence of Oken, the avatar of natural science in the German universities is still a thing of yesterday.

In 1832, Liebig admits that he has forfeited all hopes of being elected a correspondent of the Institute by publishing his opinion on the character of French chemists and on the decay of chemistry in France.

In 1833 we find Liebig denouncing the calumnies of Löwig, who had written against him a pamphlet in which the dates and the connection of certain letters were falsified. "I was," says Liebig, "for the first moment petrified at his impudence in falsehood."

In the next following letter, Berzelius is scarcely less exasperated at Brand, who has written: "Everything intelligible in Berzelius's writings is borrowed from Sir Humphry Davy." This strange and baseless assertion would be the more unwelcome to Berzelius, since it is an open secret that he had formed no favourable opinion of Davy.

Berzelius, in 1834, expresses himself on the subject of nomenclature. He holds that names should have not more than one syllable, or, at most, two syllables. "How many bad names have we not obtained by plundering the

Greek lexicon!" What would Berzelius have said had he survived to our times?

Liebig compares Mitscherlich to a leech, which sucks the blood of all it encounters and then flings them away.

In 1837 we have remarks on the contest between Pelouze and Pelletier for a vacant seat in the Academy. Both Berzelius and Liebig give their good wishes to Pelouze, whom Dumas opposes from envy, and d'Arcet from revenge. In the same year, Liebig, by occasion of a visit to England, where he says that he has "seen much, and learnt little. England is not the land of science, but of an exaggerated dilettantism. The chemists are ashamed of being called chemists because the "apotheker," who are not respected, have appropriated the name."

The chemists now, if we are to accept a decision of "Tom Brown," have no legal right to be called chemists, which is, it seems, the exclusive property of the vendors of medicines and the compounders of prescriptions. Would that they could be prevailed upon to call themselves pharmacists or pharmacutists.

Liebig, however, admits that Graham is, in a scientific point of view, a most valuable exception.

We find that in the following winter Liebig was elected a member of the Swedish Academy of Sciences. His competitors were Faraday, who obtained one vote, and Dumas, who obtained none at all! In the same season he was reconciled with Dumas, at least in appearance.

In February, 1838, Berzelius advises Liebig to cease being the "chemical executioner," and tells him that he stands so high that he does not need to tread others down.

In the succeeding letter we learn that at Mitscherlich's instigation a Ministerial decree forbade Prussian subjects to study chemistry or pharmacy at Giessen!

If we follow these letters to the end, we shall see that a coolness between Liebig and Berzelius gradually made its appearance, and in spite of the effort of Wöhler, could no longer be removed. Berzelius died in his 69th year, and Liebig in his 70th. Berzelius had gone so far as to warn students not to make themselves the instruments of Liebig.

Both these illustrious men would have regarded each other and their contemporaries with different eyes had they enjoyed good health.

Aids to Chemical Science. For Teachers and Students; more especially for those Preparing for Class "D" Examination of the New Zealand Education Department. By ANDREW GREY.

THE author dates his preface from Remuera, Auckland. The book is printed by Spottiswoode and Co., but we do not find any publisher's name, though there is a list of agents in different cities of New Zealand.

The experiments, which are well selected, illustrate the fundamental ideas of matter and energy, the conditions of matter, gravitation, mechanical powers, sound, light, heat, magnetism, electricity, chemistry, physiology, and health.

The least satisfactory portion of the book comprises the "examination papers." It is strange and sad that in our colonies the examinational system of education is adhered to with a faith truly touching.

Catechism Series.—Chemistry. Part I.: Inorganic Chemistry. Part II.: Inorganic and Organic. No Author's name. Edinburgh: E. and S. Livingstone.

PROBABLY not a few of our readers are acquainted with Hood's unfinished novel "Catechism Jack;" the hero of which is a somewhat dull youth who has been so thoroughly drilled in the Church Catechism that it supplies him with an answer to every possible question. We

were of opinion, however, that in Science, at least, this way of administering instruction had vanished with Pinnock. We hoped that teachers of all grades had become aware that the catechised student falls into the habit of correlating his knowledge with certain questions or even certain forms of questions, and consequently feels bewildered if taken out of his usual routine. Such books as those before us are undoubtedly well adapted to the examinational system, which is an unfortunate feature. It is truly painful to look over the list of publications here subjoined, and to note how many are actually praised on this account.

We fear that examinationalism, like other noxious aliens, will prove fearfully hard to banish. We can see to what a state of stagnation it has reduced its native country, China, but we close our eyes.

Would it be too much to request every author who feels tempted to write an examinational text-book to read over and digest the protest of Mr. Auberon Herbert and his friends.

Book of Chemical Labels for use in connection with Science and Art Classes. Price Ninepence.—*Book of Chemical Labels for use in the Laboratory.* Price One Shilling. Compiled by PHILIP HARRIS and Co., 144 and 146, Edmund Street, Birmingham.

Good labels are a very necessary adjunct to a laboratory, and these two books present all the most used labels in a convenient form. The type is clear, the paper good and not too thick, the gum at the back sticks well to glass, and the plan of half cutting through the paper in a continuous line enables the labels to be torn off without leaving an unsightly edge, as is the case when perforations in the postage stamp fashion are used. Plenty of duplicates of the more commonly occurring chemicals are given. "Oxalic Acid," of which there is only one solitary example in the two books, being a striking exception. Partly printed labels to be filled up in ink, according to laboratory requirements, are to be found; and a full list of standard solutions, together with several blank labels, are met with at the end of each book.

Arithmetical Chemistry. Part II. By C. J. WOODWARD, B.Sc. New Edition. London: Simpkin, Marshall, Hamilton, Kent, and Co. Birmingham: Cornish Bros.

THIS new edition is a great improvement on the previous one. The book has been entirely re-written and many additions have been made; it consists essentially of lessons on the various branches of chemistry and chemical physics, each lesson followed by a number of questions on the particular subject just explained: these should be found very useful in schools and colleges. A good index is provided, as well as a convenient table of logarithms taken from the "A B C Five-Figure Logarithms," by the same author.

Gems and Precious Stones of North America. By G. F. KUNZ. Appendix I. and II.

THE author mentions here several instances of diamonds having been found in Wisconsin and Georgia, as also in a meteorite which fell at Cañon Diablo, Arizona. These stones are of little commercial value, but they are important as bearing upon theories of the origin of the diamond. The chief deposits of this stone have hitherto been peculiar to the Southern hemisphere, or at least the equatorial region. Hence it has been surmised that they may have fallen from a flight of meteorites which crossed the more southern regions of our globe. The North American specimens, like those found in Russia, do not bear out this conjecture, though they are perfectly in harmony with the supposition of the meteoritic origin of the diamond.

Sapphires appear to have been found in Montana in the estimated quantity of 2000 ozs. per acre; but their colour is neither a true red (ruby) nor a true blue, whence they are in little request.

Turquoise is abundant in Grant County, New Mexico, and seems to have been mined for by the aborigines.

The treatise is a valuable contribution to the geographical phase of mineralogy, a science which is now very eagerly cultivated in the United States.

CORRESPONDENCE.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—The time certainly is now that an understanding should be arrived at amongst chemists by which they may be enabled to receive for their indispensable services that consideration which the dignity of their calling demands.

Such is the condition of affairs at the present moment that, although good chemists are absolutely necessary in all classes of chemical works and establishments, it is unfortunately a fact that their services are generally considered of less importance than that of the cashier or principal clerk in the office. This is made manifest by the salary offered and paid to the chemist.

An examination of the columns of such papers as are devoted to the profession will show the absurdly low salaries for which chemists are expected to devote their services and energies to their employers. Why is this? Is it because the chemical profession is undergoing retrogression? or is it because of the number of pseudo-chemists who are anxious at any price to enter into and serve an apprenticeship to practical technical work? When such a salary as £80 per annum is offered by a large corporation for a gas-works' chemist, it certainly proves that his commercial value is far and away below par.

Now, what is the reason of such a condition of things? One is prompted to think seriously that it is the result of the actions of chemists themselves; for so long as employers are able to obtain cheap labour they will continue so to do. So long as a chemist will sell himself for such a salary as an ordinary mechanic would scorn, so long will the march of the chemical profession be one of degradation.

When the Institute of Chemistry was established it was fondly hoped that it would be the means of raising to a nobly high standard those who have taken a chemical calling as a means of livelihood. But the Institute does not appear to have grasped the absolute soul of the case, and there are no doubt many men who have obtained the right to the use of the letters F.I.C., and even far higher attainments, at the present time selling the results of their hard study and long, expensive training for such a sum as £2 per week!

A remedy by which a much desired change may be brought about must be a matter to be settled amongst chemists themselves, and when once begun must not be permitted to receive a single check, but proceed steadily onwards and upwards until the goal is reached.

As a suggestion, we may form first of all a home combination, and when this is on a solid foundation invite our foreign brethren to associate themselves with us, and thus make a solid International combination. There are very few employers of chemical talent who would do otherwise than give us their utmost support.

It is not proposed to propound any set scheme in this letter, but feeling sure that chemists generally will seriously consider what they think should be done, it is left for them to criticise and formulate suggestions upon which a definite scheme may be founded.

The writer will be pleased to receive any communica-

tions on the matter, and will form one cog in the wheel which it is hoped will carry us safely and surely into a more fortunate condition of things which we honourably and rightfully claim.

If this idea is well ventilated, and if other chemists will give expression to their views in these columns, this, together with an interchange of ideas at meetings held at certain centres, would no doubt promote steady and solid progress.—I am, &c.,

T. H. DAVIS.

DISINFECTANTS—AN EXPLANATION.

To the Editor of the Chemical News.

SIR,—Will you grant me space, in order to avoid misunderstanding, to make the following explanation:—

1. I recently learned that certain samples marked "Aminol, a true disinfectant" have been sent to various gentlemen accompanied by a leaflet, in which my name, without my authority, is associated with these samples. Allow me to inform your readers that these samples contain "aminol" in water in the strength of one in five thousand. Now, the experiments which I carried out with "aminol" as regards its disinfecting power on microbes, were made with a solution of the strength of one in six hundred, and the disinfecting power of this strength was the following:—Spores of anthrax bacilli remained unaffected after eight hours' exposure; only after an exposure for twenty-four hours did the number of living spores decrease, but some escaped disinfection even after so long an exposure. Anthrax bacilli, *Staphylococcus aureus*, and others were destroyed, but only after a prolonged exposure.

2. A substance is advertised and circulated under the name of "periodate crystals," and is associated with my name without my authority. Until quite recently I have made no experiments with it. A few years ago I made a few experiments, merely of a tentative character, with a solution which was labelled "periodate," but not with the substance advertised as "periodate crystals." With these latter I have recently made experiments, and I find that their solution in full strength has no disinfecting power on microbes, pathogenic and non-pathogenic, amongst which may be mentioned the bacillus and spores of anthrax, the bacillus of typhoid and of diphtheria, of cholera and of erysipelas, the *Bacillus prodigiosus*, the *Staphylococcus aureus*, and others. Likewise I find that injection of large quantities of the solution into guinea-pigs already infected with anthrax or diphtheria has no power whatever in arresting or altering the normal course of these diseases to their fatal issue.—I am, &c.,

E. KLEIN.

ORIGIN OF THE VARIOUS COLOURS OF NITRIC ACID.

To the Editor of the Chemical News.

SIR,—My attention has been called to an article by Dr. Marchlewski upon the above subject in the *CHEMICAL NEWS*, vol. lxvi., p. 271. The writer feels himself "driven to conclude" (1) that I have only read his first communication (*Ber.*, xxiv., 3271) hurriedly, (2) that I have not read his second communication (*Zeit. Anorgan. Chemie*, i., 380) at all, and (3) that I suggest the carrying out of useless experiments.

Firstly, I can merely express my regret that I should have appeared to have read without due care the first paper by Dr. Marchlewski. Secondly, if he will kindly refer to my paper "On the Conditions of the Formation and Decomposition of Nitrous Acid" as it appears in the *Proc. Roy. Soc.*, vol. lli., p. 27, he will find that it bears the superscription "Received April 12, 1892." Dr. Marchlewski's second paper in the *Zeit. Anor. Chemie* bears

the date June 24, 1892. When my paper was sent to the Royal Society I had not read Dr. Marchlewski's second paper, for the obvious reason that it had not appeared. Thirdly, I am quite unaware that I have suggested either to Dr. Marchlewski or any other person any experiments, useless or otherwise, upon the subject.

Lastly, if in any future paper I shall have occasion to allude to Dr. Marchlewski's work, he may rest assured that I shall do so not only without criticism but without comment, as I would wish to avoid the risk of being misinterpreted and misunderstood.—I am, &c.,

V. H. VELEY.

The University Museum, Oxford.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 22, November 28, 1892.

The Existence of Distinct Nerve-Centres for the Perception of the Fundamental Colours of the Spectrum.—A. Chauseau.—The author concludes that: 1. Green, by direct demonstration, and red and violet by deduction, seem entitled, physiologically speaking, to the character of fundamental colours which has been ascribed to them by Young. 2. There are, in fact, in the nerve-centres distinct cellules for the perception of these colours, and at least endowed with three independent sensibilities—one which is excited by the vibrations of the red, another by those of the green, and a third by the vibrations of the violet. 3. These properties obscured during sleep do not resume their activity simultaneously. The aptitude for the perception of green is the first to wake up. 4. A man who has fallen asleep near a window which allows the light of the sky to fall almost equally upon both his eyes, sees, on raising his eyelids in the moment of awaking, all white or grey objects in the room momentarily illuminated with a very bright pure green. 5. The normal eye has therefore the power of analysing white light, and decomposing it into its fundamental colours. (If we have been for some time in a dark mine or cavern we see on extinguishing the tapers and stepping out into the open air all external objects illuminated with a beautifully pure green which disappears in a moment).

The Fusion of Calcium Carbonate.—A. Joannis.—The author in his experiments has kept chalk for a quarter of an hour at a temperature above the melting-point of gold. The pressure of the gases was maintained constant at about fifteen atmospheres. In two experiments in which the iron tube resisted to the end, the chalk was converted into a material comparable to marble in hardness, presenting a distinctly saccharoid fracture, but with a grain finer than that of marble. Fragments of this material are translucent along the edges. It admitted of being polished and reduced to thin laminae.

Action of Antimony upon Hydrochloric Acid.—A. Ditte and R. Metzner.—Hydrochloric acid has no action upon antimony. Hydrogen is never evolved when the two substances are brought in contact, and any antimony dissolved is due merely to the intervention of oxygen, the quantity being proportional to the weight of this gas contained in the liquids.

The Alkaline-Earth Zincates.—G. Bertrand.—The author describes the calcium, strontium, and barium zincates. The calcium salt is easily obtained by adding a saturated solution of zinc oxide to a large volume of lime water. The flocculent precipitate of calcium zincate first formed is at once re-dissolved in a large excess of ammonia, and the mixture is left under a bell-glass in

presence of sulphuric acid. The zincate is gradually deposited in crystals. The mother-liquor is decanted off, the crystals are rapidly washed in boiled distilled water and dried *in vacuo*. Their composition answers to the formula $Zn_2CaH_2O_2 \cdot 4H_2O$. The strontium and barium compounds cannot be obtained in a similar manner. The author dissolves 150 grms. strontium hydroxide in 1.5 litres hot water, adding a solution of 100 grms. zinc sulphate in 500 c.c. of ammonia (containing 10 per cent NH_3). After settling for twenty-four hours the strontium sulphate is filtered off, and the clear liquid saturated with strontia is placed under a bell in presence of sulphuric acid. A fall of temperature diminishes the solubility of the strontia, which crystallises simultaneously with zinc hydroxide and strontium zincate. The three kinds of crystals can easily be separated with forceps. The barium compound is obtained in a similar manner.

The Anhydrous and Crystalline Iron Fluorides.—C. Poulenc.—The author communicates three methods for the preparation of these compounds:—(1) The action of hydrofluoric acid upon the metals at a high temperature; (2) the action of hydrofluoric acid upon the chlorides and the oxides; (3) transformation of hydrated into anhydrous fluorides by the action of hydrofluoric acid.

Preparation of Metallic Chrome by Electrolysis.—Em. Placet.—The author electrolyses an aqueous solution of chrome-alum, to which an alkaline sulphate and a small quantity of sulphuric acid have been added. The metal is very hard and has a fine bluish white colour. It is not affected by the atmosphere and is not attacked by concentrated sulphuric acid, nitric acid, or potassa. A specimen weighing more than 1 kilo. was exhibited to the Academy.

The Preparation of Hydrobromic Acid.—E. Léger.—This paper will be inserted in full when practicable.

Reply to the Observations of M. Friedel on the Rotatory Power of the Salts of Diamines.—Albert Colson.—For this controversy we must refer to the original.

The Melting-Points of Solvents as the Lower Limit of Solubilities.—A. Etard.—This paper requires the accompanying diagrams and tables.

Researches on the Colours of Certain Insects.—Dr. A. B. Griffiths.—The wings of Lepidoptera and of other insects contain a certain number of colouring-matters. Only one true pigment has hitherto been studied, the yellow principle of the wings of some Lepidoptera (see J. G. Hopkins, *Proc. Chem. Soc. of London*, 1889, p. 117). The author has determined the composition of the green pigment in the wings of the following Lepidoptera:—*Rhopalocera*—*Papilio* (several species), *Parthenos gambrisius*, *Hesperia*, *Limentis pocris*. *Noctua*—*Halius prasinana*. *Geometra*—*Larentia* (several species), *Cidaria miata*. *Sphingida*—*Ino statice*. The same pigment is always yielded by each of these species. The wings were first treated with hot alcohol and ether, in which liquids the pigment is insoluble. The wings were then boiled in acidulated water and the filtrate was concentrated by evaporation. The green pigment deposited as an amorphous substance. The operation was repeated several times. The mean of six analyses of this green pigment gave results answering to the formula $C_{11}H_{12}N_8O_{10}$. The pigment is a bibasic acid, soluble in acids and precipitable by silver nitrate. The mean of three analyses of the silver salt leads to the formula $C_{11}H_{10}Ag_2N_8O_{10}$. The silver salt appears in silky, colourless needles very soluble in alcohol, but insoluble in ether. The alcoholic solution deflects the plane of polarisation to the right. Its specific rotatory power for the ray D is $[\alpha]_D = +29^\circ$. By prolonged boiling with water the acid pigment gives urea, alloxane, and carbonic acid. By the prolonged action of boiling hydrochloric acid the pigment is converted into uric acid. It is very probable that the green pigment is a derivative

of uric acid, and that it is deposited in the wings by the wandering cellulose, *i.e.*, it is of an excretory character. The author gives it the provisional name of lepidopterite acid. (It is to be regretted that Dr. Griffiths has not examined the absorption spectrum, if any, of this pigment).

Microbicide Action of Carbonic Acid.—Cl. Noury and C. Michel.—Milk saturated with CO_2 under pressure and kept in the cold coagulates only after the lapse of eight days, whilst ordinary milk curdles in general in forty-eight hours at the utmost. The same milk raised to the temperatures of 45° , 65° , and 80° , coagulates under the ordinary conditions. If heated to 120° it curdles at once. Carbonic acid retards the action of microbia, but it does not seem to be a true microbicide.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Sir Robert Stawell Ball, six lectures (adapted to a Juvenile Auditory) on "Astronomy"; Professor Vidor Horsley, ten lectures on "The Brain"; the Rev. Canon Ainger, three lectures on "Tennyson"; Professor Patrick Geddes, four lectures on "The Factors of Organic Evolution"; the Rev. Augustus Jessopp, three lectures on "The Great Revival—a Study in Medieval History"; Professor C. Hubert H. Parry, four lectures on "Expression and Design in Music" (with Musical Illustrations); the Right Hon. Lord Rayleigh, six lectures on "Sound and Vibrations." The Friday Evening Meetings will begin on January 20th, when a discourse will be given by Professor Dewar on "Liquid Atmospheric Air"; succeeding discourses will probably be given by Mr. Francis Galton, Mr. Alexander Siemens, Professor Charles Stewart, Professor A. H. Church, Mr. Edward Hopkinson, Mr. George Simonds, Sir Herbert Maxwell, Bart., the Right Hon. Lord Rayleigh, and other gentlemen.

The Photography of the Light Waves of the Smallest Wave-Lengths.—At the Meeting of the Mathematical and Natural Science Section of the Imperial Academy of Sciences of Vienna, on November 10th, Prof. V. von Lange presented the following communication from the engineer Victor Schumann, of Leipzig, a copy of which he has courteously forwarded us:—The photographic energy of the ultra-violet rays on collodion and gelatin plates decreases strikingly at the wave-length $200\ \mu$, and falls off to a similar extent towards the more refrangible side. The cause of this decline in energy lies in the fact which I have established spectrographically; (1) in the impermeability to light of the collodion and gelatin, in which the sensitive ingredient of the coating of the plate, *i.e.*, the silver haloid, is embedded, and (2) in the impermeability of the air which the rays have to traverse on their way to the plate. If we remove these two absorbents the silver haloid shows itself many times more sensitive for the rays beyond $200\ \mu$ than it was in presence of the collodion and gelatin, and the photographic efficacy extends far beyond the previous limit of the ultra-violet light (wave-length $185\cdot2\ \mu$). The production of a film of pure silver haloid on the plate offers great difficulties. A method for this purpose was hitherto not known. After numerous experiments I found a process by which I have now for two years prepared all the plates which I have required for observing the rays beyond the wave-length $185\cdot2\ \mu$. The air could only be removed from the rays by exhausting the spectrograph. In this manner I have hitherto been able to follow about twenty different spectra far beyond $185\cdot2\ \mu$. All of them develop here an unexpected wealth of rays, but none to so high a degree as the hydrogen light of the Geissler tube. I estimate the number of the hydrogen lines, which I have isolated at 600, and the shortest of their wave-lengths at

$100\ \mu$. I have not as yet effected the measurements, for which, however, I have already made preparations. For illustration the speaker exhibited a tableau composed of H. V. Schumann's original plates, showing the portion of the ultra-violet hydrogen spectrum first photographed by the latter.

MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
WEDNESDAY, 21st.—Meteorological, 7.
— Geological, 8.
— Microscopical, 8.

TO CORRESPONDENTS.

Muriate of Ammonia.—A German firm wishes to know the names of English firms who manufacture this article in large quantities.

ERRATUM.—P. 253, col. 1, line 33 from top, for "kalium" read "potash alum."

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THE CHEMICAL NEWS.

VOL. LXVI, No. 1726.

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

On the Earth *Ya* or *Gadolinia*.

IN the year 1878 Lawrence Smith drew the attention of chemists to the occurrence of new cerite and ytterite earths in the Samarskite of North Carolina. He extracted from them an oxide of a deep orange-yellow colour, the equivalent of which $RO=109.0$. The solutions of its salts displayed no absorption-bands. He did not sufficiently characterise this earth, the radicle of which he named *mosandrum*. Marignac and Delafontaine considered it as identical with *terbia*, the existence of which had become questionable in consequence of the researches of J. Bahr and R. Bunsen, as also of P. T. Cleve and O. M. Höglund, but was persistently upheld by Delafontaine.

An investigation of the earths of samarskite executed by this chemist showed in fact the presence of *terbia* as well as of other new earths, but he also did not succeed in their separation and distinct characterisation.

In 1880 Marignac examined the oxides of Samarskite, and obtained along with samaria (*Y₂*) an earth of an orange-yellow colour, the colourless saline solutions of which showed no absorption-bands, and the equivalent of which $RO=120.5$. It was distinguished from yttria by the slight solubility of its formate and of its double potassium sulphate, and it could not be mistaken for ytterbia on account of the greater permanence of its nitrate when heated. As Marignac considered it possible that this earth might be identical with that discovered by Delafontaine he named it provisionally *Ya*.

In 1886 W. Crookes announced that by fractionated precipitation of the earths of Samarskite with a dilute solution of ammonia, he had separated from the mean fractions an oxide showing all the properties of the earth *Ya*, and distinguished by a peculiar light-spectrum. He obtained subsequently the same spectrum from a specimen of *Ya* given him by Marignac, and ascertained that Lawrence Smith's oxide *mosandra* was a mixture of yttria with other earths, and possessed none of the properties of *Ya*. As Lecoq de Boisbaudran almost simultaneously recognised a specimen of the earth prepared by Lawrence Smith as a mixture, and as Delafontaine's supposed new earths were not confirmed, Marignac gave to the earth *Ya* the name *gadolinia*, with the symbol *Gd* for its radicle.

Lecoq de Boisbaudran then, with material supplied him by Marignac, effected careful determinations of equivalents, and described the spark-spectrum of gadolinium chloride. Some results of the researches of P. T. Cleve on gadolinia were made known by the publications of Lecoq de Boisbaudran.

Gadolinia is contained in considerable quantity in the orthites of Strömsbøe, near Arendal, as also of Hitterøe, which have furnished me the material for experiments on the cerite and ytterite earths. In a former communication I announced the method of separating samaria from *terbia* and *gadolinia*, and that there was obtained a mixture of the latter of a reddish-yellow colour contaminated merely with small quantities of samaria.

The concentrated solution of *terbium* and gadolinium nitrates, if mixed with a saturated solution of potassium sulphate, and if allowed to stand quietly, gives no pre-

cipitate of the double salts even after the lapse of many days. Precipitation occurs on violent and prolonged shaking, and is completed after a considerable time. But the earths which have remained in solution as a double salt differ but little in their equivalents, so that a separation cannot be effected in this manner. By means of a fractionated precipitation of the nitrates with dilute ammonia precipitates were at once obtained containing oxides of higher equivalent $RO=120.15$ to 120.40 , and were distinguished by a deeper colour. After a series of systematic precipitations there was finally obtained a feebly basic earth, $RO=122.0$, of a dark brown colour, consisting chiefly of *terbia*. On the other side there was obtained a more strongly basic oxide of a very faint yellowish colour, $RO=119.68$, containing especially *gadolinia*.

On a spectroscopic examination of these two earths the concentrated solutions of the nitrates showed that all traces of samaria, still contained in the final product $RO=119.96$, had accumulated in the *gadolinia* material, whilst the *terbia* material was perfectly free. For the further purification of the *gadolinia*, the solution of the nitrate was again submitted to a series of fractional precipitations with dilute ammonia, and the observation of Lecoq de Boisbaudran was confirmed that the samaria passes over in the first precipitations, and is therefore with relation to ammonia more feebly basic than *gadolinia*. The samaria was now systematically introduced into the first precipitates, and these were freed from it by treating their concentrated neutral nitrate with potassium sulphate in the manner laid down (*Annalen*, cclxiii., 165). These first purified fractions of *gadolinia* had an equivalent of $RO=119.90$, whilst the fractions last precipitated with ammonia were $RO=120.09$ to 120.16 . A spectroscopic examination showed that the latter contained mere indications of the absorption-lines of samaria, which came up rather more strongly in the fractions $RO=119.90$.

In order to obtain a *gadolinia* as free as possible from samaria, the following method was taken. All the fractions $RO=119.90$ to 120.16 , amounting to 12.3 grms., were united and dissolved in the necessary quantity of nitric acid. The solution, evaporated to a syrup on the water-bath, congealed on cooling and stirring to a colourless crystalline powder, whilst the excess of nitric acid escaped as a vapour. The saline mass was still heated for some time upon the water bath, and thus the neutral nitrate was ultimately obtained. It was dissolved in a little water and put in a 1 litre bottle containing 600 c.c. of a saturated solution of potassium sulphate and a considerable quantity of the same salt in the state of a fine powder. The whole was allowed to stand for three days with frequent violent agitation, and the solution was filtered off from the double salt which had been formed and from the undissolved excess of potassium sulphate. The volume of the filtrate was measured, the earth separated from it was weighed, and its equivalent was determined. The earth separated from the precipitated double salt was also separated, and with it the same procedure was repeated. Thus two constants served as a measure for the unity and purity of the earth, *i.e.*, its equivalent, and the proportion of solubility in a saturated solution of potassium sulphate, which latter value must be constant for a unitary salt at one and the same temperature.

Fraction I.—1.0682 grms. *gadolinia* yielded 1.7779 grms. gadolinium sulphate, $RO=120.20$, $R_2O_3=360.60$.

Fraction II.—1.0580 grms. *gadolinia* yielded 1.7611 grms. gadolinium sulphate, $RO=120.17$, $R_2O_3=360.51$.

Fraction III.—1.0796 grms. *gadolinia* yielded 1.7969 grms. gadolinium sulphate, $RO=120.19$, $R_2O_3=360.57$.

(To be continued.)

Fusion of Calcium Carbonate.—H. Le Chatelier.—The author, unlike M. Joannis, finds that the fusion and crystallisation of precipitated calcium carbonate may be produced by heat alone without the intervention of an elevated pressure.—*Comptes Rendus*, cxv., No. 23.

* From Liebig's Annalen.

THE ABSORPTION OF ATMOSPHERIC NITROGEN BY VEGETATION.

As the long discussion concerning the source of the nitrogenous matter of plants seems to be drawing to a close, it may be useful to summarise the successive stages of the dispute, and to show the conclusion towards which Science and practice are jointly tending.

In 1849 it was generally admitted,—to no small degree on the faith of the experiments of M. Boussingault,—that plants derived their nitrogen either from nitrogenous manures or from the ammonia present in the atmosphere. In the same year M. Georges Ville, experimenting upon lupins and cress, found that whilst the plants had absorbed 103 m.grms. of nitrogen, the air had scarcely introduced 1 m.grm. of nitrogen into his apparatus in the form of ammonia.

Entering upon a very extended series of determinations of the ammonia in the air, he arrived at the conclusion that it contains on the average 23.11 grms. of ammonia per million kilos. Twenty-six years later M. Schloesing undertook the same determination, but instead of one million kilos. he took as his unit 100 cubic metres, in which he found 2.56 m.grms. of ammonia. Hence no comparison of his results with those of M. Ville was possible without a previous calculation. But on reducing both these results to the same standard (100 cubic metres of air), it appears that the difference between the two determinations is trifling. We have according to—

G. Ville	2.84 m.grms.
Schloesing	2.56 „
Difference.. ..	0.28 „

The difference, therefore, in 130 kilos. of air is merely 2.10ths of 1 m.grm. M. Schloesing, however, still assumes the attitude of the first and true determiner of the quantity of ammonia in the air.

As far back as 1849 M. Ville also established the fact that atmospheric nitrogen is absorbed by cress. This fact has been indeed denied, but it has been fully confirmed by M. Bréal (*Annales Agronomiques*, xviii., p. 269) and M. P. P. Dehérain. MM. Schloesing, jun., and Laurent have since shown that certain of the lower plants are capable of fixing free nitrogen, and Professor Berthelot has proved the same fact as occurring during the growth of the amarantus. Hence the first part of the question may be regarded as decided: plants are able to take up and utilise the free nitrogen of the atmosphere.

But now comes the second problem; by what means is the nitrogen taken up and assimilated? It was proved by certain observers—Prof. Berthelot and HH. Hellriegel and Willfabrt—that the process depended on the activity of microbia. These minute beings were found on the surface of the soil, but more especially in nodules on the roots of leguminous plants, such as kidney-beans, peas, lupins, &c. It was found that those plants whose rootlets were most beset with these tubercles were least dependent upon nitrogenous manures, since by the mediation of the microbia they were able to draw their supply of nitrogen direct from the atmosphere. In some cases nitrates or ammoniacal compounds may interfere with the development and activity of the microbia, and thus hinder the growth of the crop. The lupins yield the best crop without the application of a nitrogenous manure, which if applied to them is wasted. Peas are less able to dispense with nitrogenous manures, as is also the case with clover.

But we can now take a third and final step. The action of the microbia to which we have referred is unquestionable, but it is not the only agency by which plants are able to appropriate atmospheric nitrogen. Franks has shown that plants other than leguminous are capable of effecting the fixation of nitrogen without the co-opera-

tion of microbia. He has cultivated oats, buckwheat, asparagus, colza, &c., in different soils, and finds that they can assimilate nitrogen without the aid of microbia, and of course without belonging to the leguminous class. They are able to produce organic nitrogen without impoverishing the soil, which, on the contrary, is rather enriched. Hence we see that Georges Ville's "sideration" is no subject for derision, but has its rational basis at once in practice and in Science.

ON THE MAGNETIC ELEMENTS FOUND IN ROCKS AND MINERALS.

By Dr. T. L. PHIPSON, F.C.S., &c.

IN addition to what has been stated on this subject by Prof. Liversidge in his interesting papers published recently in the *CHEMICAL NEWS*, perhaps I may be allowed to claim having first called attention to the presence of magnetite in the red hæmatite ore of Waldeck, Germany, as early as 1865. Since then I have many times found that the magnet extracts a notable amount of magnetic oxide from some English ironstones of a similar nature. But a more surprising result was obtained not very long ago whilst I was examining some Hungarian syenite rocks containing here and there specks of iron pyrites, and yielding to analysis a minute quantity of gold. From the pulverised rock the magnet extracted a dark coloured substance which dissolved in hydrochloric acid with evolution of hydrogen sulphide, and was proved to be magnetic pyrites.

I believe that a certain alloy of iron and platinum, said to exist in primitive rocks, can also be extracted in this manner. Rocks pulverised in iron mortars will almost always yield metallic iron particles in notable amount to the magnet, so that copper mortars must be used in such experiments.

Analytical Laboratory, Putney,
London, December 10, 1892.

NOTE ON MR. DOHERTY'S ANALYSIS OF THE BANANA.

By Dr. GEORGE LAWSON,

Professor of Chemistry, Dalhousie University, Halifax,
Nova Scotia.

MR. DOHERTY, of the Assay Department, New South Wales, has done good service in making and publishing, in the *CHEMICAL NEWS*, an analysis of the banana fruit. He shows that the peeled fruit of *Musa Cavendishii*, which contains 75.71 per cent of water, yields:—

Albumenoids	1.71 per cent.
Starch	5.90 „
Sugar	3.00 „
Carbonaceous matter ..	11.24 „

An extension of Mr. Doherty's work into greater detail as regards the carbohydrates would be valuable.

From a chemico microscopical examination of the banana made many years ago (the notes of which have not been published), I ascertained that at the period of maturity of growth of the fruit (while still unripe) its constituent cells were densely filled with starch granules, which are elongated and of characteristic form. As the fruit ripened, the starch granules gradually disappeared, dissolving away into sugar, so that in the perfectly ripe fruit, or in the perfectly ripe pulpy portions of a fruit, there was little or no trace of visible starch. In other words, at the stage of simple maturity the carbohydrate cell-contents of the fruit consist entirely, or almost so, of

starch; while at perfect ripeness they are converted into sugar.

It would be interesting to have—(1) a careful determination of the actual amount of starch present in the mature fruit before commencement of the ripening process; and (2) a similar determination of the sugar at the period of perfect ripeness. The determinations should be made from fruits taken from the same bunch of the living plant. It does not grow here.

I presume Mr. Doherty's item—"carbonaceous matter (non-nitrogenous), 11.24"—represents principally cellulose, which seems large (in addition to woody-fibre, 1.74) for the peeled or pulpy part of such a succulent fruit, inasmuch as the starch and sugar together make scarcely 9 per cent. The proportion of sugar in the fruit at ripeness may be expected to be less relatively than the starch at the initial stage of ripening.

NEW METHOD OF PRODUCING GEMS ARTIFICIALLY.

By JAMES MORRIS, D.Sc.(Tüb.).

(Continued from p. 71).

IN this article I shall deal further with the chief product of the process, namely, the crystals of alumina. In how far these crystals may be termed sapphires, or in how far only crystallised alumina, is not within the scope of the present paper.

It is known that the African diamonds differ in certain physical qualities from those of Brazil and India. When carbon crystals come to be produced artificially in numbers they will most probably differ physically from the products of all known mines. I presume that they would still be termed diamonds.

Towards aqueous solvents the crystals obtained by my process show great resistance, many of them having been heated in sulphuric acid for days. Towards fluxes they appear to be somewhat more easily attackable than would certain varieties of the natural stones, although the fact of their having been, in some cases, previously subjected to long heating in acid may have lowered their power of resistance.

On fusion with microcosmic salt they disappeared with very great difficulty. There was no appearance of silica. No great excess of salt was used. (The crystals had been previously tested both with hydrofluoric acid and with fluoride of ammonium). On fusion with borax they disappeared with rather more ease. The authorities vary in regard to the solubility of silica in borax. However, quite apart from the question of silica, the borax was used in many tests as being less liable to cause oxidation of the carbon in the crystals than microcosmic salt might have been.

This question of the carbon in the crystals,—carbon presumably in the diamond form,—is so remarkable that even on the evidence obtained I might hesitate to lay so much weight on it. I previously referred to the work of C. Greville Williams (*Proc. Roy. Soc.*, xxi., 1872-3, also in "Ures' Dictionary," and in *Encyc. Britt.*), and to the recent experiments of Luzi. The latter observer (*Ber. Deutsch. Chem. Gesell.*, 1891, p. 4093) heated mineral matter to fusion in contact with lamp-black, and he found on cooling that a portion of the carbon had assumed the form of graphite. He seemed to entertain the possibility of a real solution of the carbon in the mineral matter, with subsequent elimination in the graphitic form. It is at least possible that, under certain conditions of cooling, a portion of the carbon would have been retained in the mineral matter. In this communication Luzi brings the results of his experiments to bear on certain geological phenomena both general, specific, and local.

In a later paper (*Ber. Deutsch. Chem. Gesell.*, 1892, p.

2470), the same experimenter describes how he placed a diamond in a quantity of the "blue ground" (obtained from South Africa), and heated the latter to fusion. On subsequent examination he found that a large portion of the diamond had disappeared, and he did not seem to attribute such disappearance to any air which might have found its way to it, but to magmatic re-absorption. In this case, however, he entertains the possibility of the diamond carbon having been used to effect a reduction in the mineral matter.

Particles of graphite are found in gneiss, porphyrite, marble, and other rocks and rock masses. All this tends to show that the line of absolute insolubility is very difficult to determine.

I shall now proceed to one of the chief parts of the present communication, namely, the manner in which the crystals were obtained. The crystallising agent used was a very simple and natural one—to wit, carbonic acid gas, and at this point we go back to the first of all chemical-geological experiments.

About a hundred years ago Sir James Hall (*Trans. Roy. Soc., Edinburgh*, 1812, p. 71, 185), effected the transformation of limestone into marble, and the means which he used was the simple one of heating the substance in a closed vessel, and keeping the carbonic acid in. The object which he had primarily in view had nothing to do with mineral synthesis, so the considerations involved in this experiment need not be gone into at length here. He seemed, however, to regard the transformation as having been accompanied by actual fusion.

The experiment was repeated by Gustav Rose (*Mon. Ber. Berl. Akad.*, 1862, p. 669), by Becker (*Tschermak's Min. Mittheil.*, Heft i., 1885), and by Doelter (*N. J. F. Min.*, 1886, p. 133). The latter observer found that there was no real fusion, but a regeneration, and the last mentioned mineralogist got similar results by using not a closed vessel, but a tube open at one end and leading carbonic acid gas over the carbonate. Pressure is therefore not necessary. This last point is practically important. Similar experiments were successfully made with magnesite. The reason why carbonic acid gas effects the crystallisation of these carbonates, or of alumina, need not be considered at this stage.

In my experiments the gas was not made to act simply on the loose powder, but under the following conditions. Pure alumina was dissolved in pure hydrochloric acid, and a mixture of lamp-black and charcoal was added to the solution. The mass was evaporated, and the alumina was precipitated in the pores of the carbon. The mixture contained by weight rather more carbon than alumina. After further treatment to expel all the hydrochloric acid, the mixture was subjected to the action of carbonic acid gas at a red heat. The largest vessels used were the iron retorts which were formerly often employed in making oxygen gas from black oxide of manganese. They are about one foot high, and three or four inches wide. Very promising results were obtained in one inch iron tubes, heated in Fletcher tube furnaces. In this case the carbonic acid gas was heated alone before being passed over the mixture. The latter was, of course, also directly heated. In future working some equivalent disposition of the apparatus will be reverted to.

The mixture of alumina and carbon was at first rolled into balls, but as the retorts had to be opened at intervals for examination, the balls mostly broke down into fragments. This is a matter of mechanical arrangement. The lamp-black interlocked a large amount of the oxide, and the charcoal maintained the permeability to the gas. The gradual consumption of the carbon in the carbonic acid gas is, in an indirect way, equivalent to the removal of the solvent in cases of crystallisation from solution. By using a suitable mixture of lamp-black and charcoal, and by stopping the combustion at the proper point, the mass assumes a honeycombed structure which forms a matrix in which the alumina crystallises.

The best result was obtained on continuing the opera-

tion to what would be about the equivalent of one month's continuous heating. A very moderate red heat was employed. The factors of time and temperature are interchangeable within considerable limits, and in other cases crystals were obtained in very much less time. The experiments in the tubes proceeded rapidly. Many of the crystals obtained by the process were about 1 m.m. in diameter, some larger, and measurable crystals were found in thousands.

For an experimental process, often interrupted, and performed in extemporised apparatus, I think that the result may be pronounced distinctly favourable. Had experimental tube furnaces of proper size been obtainable I should not have used retorts.

Various precautions were taken in regard to the purity of the alumina, the acid, the carbon, and the carbonic acid gas. A very small amount of moisture in the gas seemed to be favourable. The carbon must be what could be termed "dry," that is, it must contain no tarry matter. There were in the product a few crystals which, from their shape, also from other considerations (reducing actions take place in the vessels), may possibly be a new oxide of aluminium. It is strange that no oxide corresponding to the magnetic oxide of iron has yet been found. Several observers have obtained indirect evidence of a lower oxide of aluminium having been formed, and its isolation is almost a certainty of the future.

There are many more interesting points connected with the chemical and physical, and more particularly crystallising, effects of carbonic acid gas, which I shall probably go into in a further communication.

In a paper of the present kind it is scarcely possible, and I certainly do not consider it desirable, to dissociate the chemical from the geological aspects of the question. One of the most important points of all is: in what degree, if at all, does the process described resemble the process of nature. In this connection we have the broad but still very relevant fact that carbonic acid is really found in many minerals, including quartz, topaz, and sapphire. I need hardly refer to all the literature, both special and allied, including the names of Brewster, Sorby, Simmler, Vogelsang, and many other and more recent observers. Certainly the fact cannot be overlooked that, in some of these crystals the carbonic acid is present in the liquid form.

In Quenstedt's "Mineralogie," article "Feldspath," he says (although it is not quite clear whether he speaks in his own name or quotes another author):—"Wasserporen mit beweglichen Bläschen in Feldspath des Basaltes von Lichtenberg in Franken (*Fahrb.*, 1867, p. 701), beweisen nur, dass auch im Feuer unter Druck Flüssigkeiten nicht fehlen." Professor Quenstedt was geologist, physicist, and mathematician. I do not know what attempts have been made to bring certain petrological phenomena into line with the known facts and accepted theories regarding temperatures, critical points, and pressures. As already stated in another sense, the factors of time and of temperature, also of pressure, seem to be largely interchangeable. Certainly Doelter's modification of Hall's original experiment shows that the importance of pressure may be overrated. It is quite possible that the rubies and sapphires of nature have been produced by more than one process.

Apart from the presence in various crystals of lacunæ, containing carbonic acid, the natural occurrence of the noble crystals of alumina is, in some cases, suggestive. According to Tennent, the matrix of the small rubies, mostly light coloured, found in Ceylon, is dolomite. Clear crystals, both blue and rose-coloured, are found in the saccharoidal dolomite at St. Gothard. Emery is found in granular limestones and dolomites in Naxos and other places.

The use of the carbon in my process may be less natural than the use of carbonic acid gas. Carbonaceous matter is not uncommon in rocks and minerals. It may also be that the carbon takes the place of one of the

undetermined physical factors which go to constitute the process of nature.

I venture to think that in the use of carbonic acid we have promise of a natural, simple, and effective instrument in unfolding certain problems in connection with the genesis and metamorphosis of many minerals. It also gives promise of the effectual synthesis of some of the noblest of them.

217, West George Street, Glasgow,
November, 1892.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Continued from p. 287).

Copper from Cadmium.

Copper taken.	Cadmium taken.	Metal deposited.	Free acid.	H ₂ O. C.c.	OH gas per min. C.c.	Time. Hrs.	Diff. from theory. Perct.
0.1074	0.0984	0.2061	10	100	0.8	17	—

This result was not unexpected, considering what we have already learned in regard to the behaviour of these metals. The deposit was very dark and spongy. Both metals were completely precipitated. Two subsequent experiments were equally unsatisfactory; in one the current was reduced to 0.3 c.c. OH gas per minute; in the other, 25 c.c. of formic acid was added. No separation was effected.

Copper from Iron.

Copper taken.	Iron taken.	Copper found.	Free acid.	H ₂ O. C.c.	OH gas per min. C.c.	Time. Hrs.	Diff. from theory. Perct.
1. 0.1057	0.1248	0.1035	25	125	0.8	20	—
2. 0.1057	0.1248	—	25	150	0.8	42	—
3. 0.1057	0.1248	0.1019	25	150	0.8	19	—
4. 0.1057	0.1248	0.0999	25	150	0.8	17	—
5. 0.1057	0.1248	0.1014	25	150	0.8	18	—

Although free acid was present in considerable quantity (25 c.c.), the formate of iron in the solution was decomposed with the formation of ferric hydrate, which separated as a light yellow froth on the surface of the solution. It also formed crusts at the edge of the copper deposit, which adhered to the dish with such tenacity that all attempts at removal by mechanical means were failures. Mere washing was without avail, and more energetic measures resulted in a loss of copper (1 and 4). Dilute hydrochloric acid was added to 2; but, while it dissolved traces of copper, it failed to remove the deposit of iron hydrate. Dilute sulphuric acid was also tried without success (3). In the final determination 20 c.c. of concentrated oxalic acid was added at the end of seventeen hours, and the current allowed to act one hour longer. The froth floating on the surface was dissolved, but the deposit on the copper was not appreciably affected. Except at the periphery the copper had a bright metallic lustre and was firm and adherent.

Cadmium from Iron.

Cadmium taken.	Iron taken.	Cadmium found.	Free acid.	H ₂ O. C.c.	OH gas per min. C.c.	Time. Hrs.
1. 0.0984	0.1248	0.0996	25	150	0.8	23
2. 0.0984	0.1248	0.1021	25	150	0.8	45

The same trouble was experienced here. Similar attempts were made to remove the iron, but without

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxxi., No. 136.

success. In the first of the above determinations 10 c.c. of oxalic acid solution was added before the conclusion of the experiment; in the latter, 20 c.c. of the same solution.

The hydrate of iron in the solution disappeared, but adherent crusts still remained on the surface of the cadmium.

Zinc from Iron.

Several tentative experiments were made, but as the iron showed the same tendency to separate on the sides of the dish, as in the preceding determinations, they were not continued.

Copper from Cobalt.

Copper taken.	Cobalt taken.	Copper found.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Percent.
1. 0'1101	0'1080	0'1105	100	175	1	21	+0'36
2. 0'1101	0'1080	0'1095	100	175	1	17	-0'54
3. 0'1101	0'1080	0'1097	100	175	1	17	-0'36
4. 0'1101	0'1080	0'1107	100	175	1	18	+0'54
5. 0'1101	0'1080	0'1098	100	175	1'2	17	-0'27
6. 0'1101	0'1080	0'1097	100	175	1	16	-0'36

On attempting to prepare a solution of cobaltous formate for the above determinations, it was found that the salt made according to the method already described was not readily soluble in water. The solution was therefore prepared by double decomposition as follows:—500 c.c. of water containing 6'563 grms. of sodium formate was mixed with an equal amount of water in which 8'728 grains of cobalt chloride had been dissolved.

Of this solution 50 c.c. was taken, containing 0'1080 grms. of cobalt. The distance between the poles was 3'8 c.m., except 1 and 4, in which it was 2'8 c.m. Both of the latter were spongy; the others slightly so. As the conditions otherwise were similar, the difference in the character of the deposits was apparently due to the separation of the poles. Traces of cobalt were found in all the copper deposits. The copper was all out except in 3, 5, and 6, in which the solutions were coloured yellowish brown on the addition of hydrogen sulphide.

The copper deposit was dark in colour and adherent, although not very compact on the bottom of the dish.

Copper from Nickel.

Copper taken.	Nickel taken.	Copper found.	Free acid.	H ₂ O.	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Percent.
1. 0'1101	0'1028	0'1095	75	175	1	20	-0'54
2. 0'1101	0'1028	0'1097	100	175	1	17	-0'36
3. 0'1101	0'1028	0'1097	100	175	1	18	-0'36
4. 0'1101	0'1028	0'1098	100	175	1'2	17	-0'27
5. 0'1101	0'1028	0'1096	100	175	1	17	-0'46
6. 0'1101	0'1028	0'1098	100	175	1	17	-0'27

The same trouble was experienced in preparing a satisfactory solution of pure nickel formate as with cobalt, and it was found advisable to prepare the solution by double decomposition in the same way as the latter salt; 500 c.c. of this solution contained 8'3077 grms. of nickel chloride and 6'2469 grms. of sodium formate. In both cases a slight excess of sodium formate was used. The copper contained traces of nickel, and slightly coloured the solution when tested with hydrogen sulphide. The conditions were similar to those given under cobalt, and the results were quite as satisfactory. The copper was bright and compact.

(To be continued).

Determination of the Acidity of Milk.—H. C. Plaut (*Archiv. f. Hygiene*).—For determining the acidity of milk, the author prefers a modification of Soxhlet's original volumetric process. He titrates 50 c.c. of milk with $\frac{1}{2}$ normal solution of baryta, using phenolphthalein as indicator.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 1st, 1892.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

(Concluded from p. 300).

*75. "The Origin of Colour. VI. Azobenzene." By HENRY E. ARMSTRONG.

A compound represented by the formula $C_6H_5 \cdot N:N \cdot C_6H_5$ obviously does not come within my "colour rule," and should, in fact, be colourless; yet azobenzene is a brilliantly orange-red coloured substance; moreover, the formula usually attributed to the diazo-salts, e.g., diazobenzene chloride, $C_6H_5 \cdot N:N \cdot Cl$, represent these as comparable in constitution with azobenzene, yet they are colourless; hence I have long doubted the correctness of the formula attributed to azobenzene.

Werigo, in a paper, "Ueber die Additionsfähigkeit des Azobenzids" (*Annalen*, 1872, clxv., 189), has drawn attention to the readiness with which azobenzene forms addition compounds, and describes a hexabromide; he also states that it affords a colourless tetrabromo-substitution derivative. At my request, Mr. E. Mills has undertaken to revise Werigo's observations, and to study the bromo- and other derivatives of azobenzene in detail, as these promise to be of considerable interest.

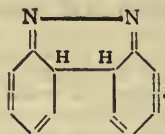
It appeared not improbable that Werigo's hexabromide belonged to the diazo-perbromide class, but this, it seems, is not the case; by treating it with ammonia, Mr. Mills has obtained only bromo-substitution derivatives of azobenzene—chiefly diparabromazobenzene—no azoinide being formed (*cf.* Meldola and Hawkins, *Proc. Chem. Soc.*, 1892, 133). He has confirmed Werigo's statement that when bromine acts on a hot alcoholic solution of azobenzene, a colourless tetrabromo-derivative is produced, which, on reduction, yields a tetrabromobenzidine apparently identical with that prepared from benzidine by Claus and Risler; and as he has not succeeded in obtaining the colourless tetrabromo-compound from diparabromazobenzene, there can be little doubt that none of the bromine atoms in the tetrabromo-derivative are in para-position to the nitrogen atoms.

Experiments made with the object of preparing alkyl derivatives of hydrazobenzene have hitherto been unsuccessful; when boiled with zinc chloride and alcohol it yields benzidine.

As the introduction of bromine into a coloured compound usually has the effect of heightening the colour, the conversion of azobenzene into a colourless bromo-derivative would seem to indicate that in some way the type changes; the tetra-derivative may well be a compound of the formula $C_6H_3Br_2 \cdot N \equiv N \cdot C_6H_3Br_2$.

The formula generally attributed to azobenzene may, therefore, be regarded as unsatisfactory not only because it is a coloured substance, but also because it combines with bromine, &c., with a readiness which is unusual in the case of mono-derivatives of benzene; because it yields a considerable proportion of a meta-monobromo-derivative, and of a higher bromo-derivative in which, apparently, none of the bromine atoms are in para-positions, an altogether unusual circumstance in the case of benzene mono-derivatives other than those containing acid radicles; and because it yields a colourless tetrabromo-derivative.

The following formula would "account" for all these peculiarities, and in a measure "explain" the formation of benzidine and diphenylene as well as the recent remarkable observations on the production of diphenylamine derivatives from azobenzenoid compounds on reduction; but it is eminently unconventional, and its adoption involves the recognition of a form of interaction not yet entertained by chemists:—

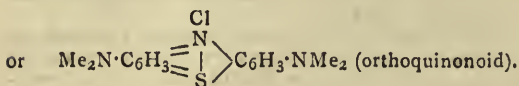
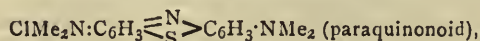


DISCUSSION.

Mr. GREEN considered that the relation of constitution to colour was a very important question both from a theoretical and practical point of view. The "quinonoid" hypothesis advocated by Dr. Armstrong appeared to him to be the only satisfactory attempt which had been hitherto made to formulate a complete theory of chromogenesis. Witt and others had given us chromophores, chromogens, and auxochromes, but these ideas were more names than theories, as no one had yet been able to predict what groups would be chromophores and what not. The "quinonoid" hypothesis, however, put us fairly on the road to predicting whether a compound of a certain constitution would be a dye-stuff or not, and might even eventually lead to the prediction of the shade and dyeing properties. He had given a good deal of attention to the subject recently, and although he had begun by regarding the "quinonoid" theory in a somewhat sceptical light, it had recommended itself to him more and more, as he found so many facts, hitherto inexplicable, which were explained perfectly simply by its means. He might instance the formation of rosaniline in the magenta-melt, which was readily explained by assuming the primary formation of an oxidation product of paratoluidine, viz., $\text{H}_2\text{C}:\text{C}_6\text{H}_4:\text{NH}$, which might then undergo alternate additions of aniline and reoxidations. He believed he had obtained this parent substance of the rosaniline series by oxidation of paratoluidine sulphate in acid solution, and it appeared to be identical with a substance described by Dr. Perkin as an isomer of paratoluene. Again, the well-known tendency of quinones to form substituted amidoquinones with amines explains the ready formation of such complicated products as safranin, the indulines, aniline-black, &c.

He was inclined rather to attribute the cause of the colour in such "quinonoid" compounds to a strain set up within the benzene nucleus by two of the bonds ceasing to act centrally, than to the arrangement of these bonds outside the nucleus, i.e., as *intra*-nuclear rather than *inter*-nuclear.

On the "quinonoid" hypothesis, two groups of colours should be possible, viz., "ortho-colours" and "para-colours." The colours of the rosaniline series can only be formulated as para-colours, indigo only as an ortho-colour. On the other hand, many of the artificial colouring matters may be viewed either as para- or ortho-colours; thus methylene blue may be written:—



The speaker had recently examined a large number of colouring matters in regard to their behaviour towards reducing agents and the stability of their leuco-compounds, and had brought to light the remarkable fact that, whereas the leuco-compounds of the rosaniline, aurin, and phthalein colours were very stable, resisting air oxidation, the opposite was the case with the leuco-colours of the azine, oxazine, thiazine, acridine, safranin, and induline series, which all oxidise in the air to the corresponding colours with extreme rapidity. This was also the case with leucindigo and its sulphonic acid. The conclusion seemed to him to be irresistible, that the colours of the latter class were *ortho*-colours, whereas the eosines, aurines, rhodamines, &c., like the rosanilines, were *para*-colours.

Mr. FRISWELL agreed that confirmation of Dr. Armstrong's views was afforded by facts such as, for example, the colourlessness of triamidotriphenylcarbinol in comparison with the intense colour of its anhydro-base, which could be represented by a quinonoid formula. He, however, thought that the representation of colour as characteristic of a particular constitution was, for many reasons, to be deprecated, and that the remarkable effect of molecules external to the potential colour molecule in either developing or suppressing colour required attention. In the case of trihydroxytriphenylcarbinol, an apparently colourless substance, colour was developed by alkali, the salts being powerfully coloured; and in the case of the interesting dye "pure scarlet" discovered by E. C. Nicholson, which the speaker had himself studied, and which he thought was to be represented by the formula $\text{HO}:\text{C}(\text{C}_6\text{H}_4\text{:OH})_2(\text{C}_6\text{H}_3\text{MeNH}_2)$, both acid and alkali salts were coloured, although the substance itself was but feebly coloured.

The sulphonic acids of triphenylrosaniline were powerful colours, but their combinations with alkalis almost colourless; so that wool dyed with the sodium salt of Nicholson-blue was nearly white until dipped into acid. This phenomenon was even more marked in Meldola's alkali-green.

In illustration of the fact that substances exactly similar in constitution behaved in remarkably dissimilar ways, the following experiment was then made:—Two tubes were taken: one contained rosaniline base, benzoic acid, and aniline, the other triphenylrosaniline base, benzoic acid, and aniline—the latter being of an intense blue, the former a feeble red, colour. On heating to a similar temperature, the rosaniline base combined with the benzoic acid, and the well-known magenta colour was produced in the one tube; while in the other the triphenylrosaniline base split off from the benzoic acid, and only the dull brownish feeble colour of the base was noticeable. These facts showed:—(1) The importance of factors external to the potential colour molecule; (2) the variations of behaviour of substances containing similar potential colour molecules. Hence, he considered time not yet ripe for extensive generalisation as to the origin of colour in the benzene series.

[Mr. Friswell's argument is valid only if proof can be given that the coloured salts he refers to are *carbinolic*; there is no reason to suppose at present that the change which attends the formation of the rosaniline salts does not occur in all the cases he mentions in which coloured compounds result.—H. E. A.]

Mr. JACKSON enquired whether the vapour of quinone were coloured.

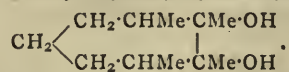
Mr. LING mentioned that diparaiodobenzene had but a pale yellow colour.

76. "The Reduction Products of Dimethyldiacetylpentane." By F. STANLEY KIPPING, Ph.D., D.Sc.

It is shown that dimethyldiacetylpentane,—



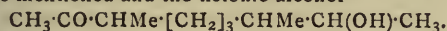
a diketone produced by the hydrolysis of ethylic dimethyldiacetylpinelate (Kipping and Mackenzie, C. S. Trans., 1891, 569), is readily converted by reduction into a mixture of approximately equal quantities of dimethyldihydroxy-nonane, and of a compound which, judging from the manner in which it is formed, may, it is thought, be regarded as tetramethyldihydroxyheptamethylene,—



When the crude products obtained by heating a moist ethereal solution of the ketone with sodium is submitted to steam distillation, a colourless oil, which has a peculiar and characteristic odour, slowly passes over, leaving as residue an almost odourless, practically non-volatile oil.

Excluding pinacones and other condensation products which might be formed, and which would be characterised

by a very high boiling point, only three compounds can be produced by the reduction of the diketone, namely, the above mentioned and the ketonic alcohol—



As the non volatile oil has the composition $\text{C}_{11}\text{H}_{24}\text{O}_2$, and yields a diacetyl derivative of the composition $\text{C}_{11}\text{H}_{22}\text{O}_2\text{Ac}_2$, it is to be regarded as dimethyldihydroxy-nonane.

The volatile oil is not reduced on treatment of its solution in moist ether with sodium, and is not acted on by phenylhydrazin or hydroxylamine; hence, it cannot be a ketonic alcohol of the constitution given above; it would appear probable, therefore, that it is a tetramethyldihydroxyheptamethylene. This conclusion is borne out by the great similarity in properties between the volatile oil and the dimethyldihydroxyheptamethylene previously described by Kipping and Perkin (*C. S. Trans.*, 1891, 214), a resemblance which cannot fail to be observed when working with the two compounds.

77. "The Products of the Interaction of Zinc Chloride or Sulphuric Acid and Camphor." (Third Notice). By HENRY E. ARMSTRONG and F. S. KIPPING.

In a previous notice (*Proc. C. S.*, 1892, 54), in which it was shown that the crude product obtained on heating camphor with either sulphuric acid or zinc chloride contains 1:2:4-acetylorthoxylene, reference was made to the presence of a constituent to which presumably the oil owes its strong, peppermint-like odour; all attempts to separate this constituent by fractional distillation were unsuccessful, nor could it be removed from the oil from which the acetorthoxylene-hydrazone had been separated by crystallisation. As it was observed that the crude oil readily decolourised an acid solution of permanganate, which has but little action on camphor and acetorthoxylene, a quantity of the oil from which these latter had, as far as possible, been separated was submitted to oxidation; ultimately an acid was obtained which has proved to be α -methylglutaric acid. As this acid is the characteristic oxidation product of the phorone obtained by distilling calcic camphorate, according to Königs and Eppen, which has a strong peppermint-like odour, it is very probable that a homologue of this phorone is present in the camphor product, which has a higher boiling point than camphorone.

79. "The Griess-Sandmeyer Interactions and Gattermann's Modification thereof." By HENRY E. ARMSTRONG and W. P. WYNNE.

Having frequently had occasion, during several years past, especially in the course of our studies of naphthalene derivatives, to avail ourselves of the marvellous improvements effected by Sandmeyer in the Griess methods of displacing the amido-group by halogens, &c., we have been led to carefully study the conditions requisite for success, and have long since come to the conclusion that, in very many cases, much better results may be obtained by operating at relatively low temperatures instead of at the boiling point as recommended in most cases by Sandmeyer. Experiments made at the request of one of the writers by Mr. Conroy with the object of comparing the yield in the case of the conversion of aniline into chloro- and cyano-benzene when operating:—

- 1, in accordance with Sandmeyer's original directions;
- 2, in accordance with Gattermann's directions, using finely-divided copper in place of cuprous salt;
- 3, in general accordance with Sandmeyer's directions, but at lower temperatures,

have led to the conclusion that, in the case of chlorobenzene, an infinitely better yield is obtained by mixing the cooled cuprous with the cooled diazo-solution, subsequently allowing the temperature to rise. It appears also that the Gattermann process affords a larger yield only in so far as it differs from the Sandmeyer process by being carried out at a lower temperature, and that it differs in no other essential particular from the Sandmeyer pro-

cess; there is, in fact, an entire absence of evidence that the copper acts as such, or except it has undergone conversion into cuprous salt. In the case of cyanobenzene, apparently the same advantage is not derived from carrying on the operation at a low temperature.

The "cold process" has been found to be of advantage in many other cases. Several years ago, the preparation of large quantities of orthochlorotoluene was carried out in the Central Institution Laboratory essentially in the manner described by Erdmann in his recent paper in *Liebigs Annalen*, and the yield was even better than that he obtained. Allusion is made to this in the paper by one of us on toluene derivatives (*cf. Proc. C. S.*, 1892, 139) which appears in the December number of the *Transactions*; several other instances of the application of the cold process are mentioned there.

We are entirely in accord with Erdmann as to the different and peculiar behaviour of the cuprous compounds of various diazo-derivatives; it is especially noteworthy in the case of naphthalene derivatives that the temperature at which nitrogen is evolved varies for each compound, and that there is a temperature optimum at which the conversion should be effected to obtain the maximum amount of pure product. There is no comparison, especially in the case of the naphthylaminesulphonic acids, between the two methods, colourless products being readily and almost immediately obtained by decomposing the diazo-cuprous compound at the favourable temperature, whereas on heating to the boiling point coloured products, which obstinately resist purification, are obtained. There can be little doubt that the formation of "azobenzenes," to which Erdmann directs attention, is, at least, very largely the cause of this colouration. The difficulty met with in converting betanaphthylamine into betachloronaphthalene, which Gattermann has specially noticed, is not got over by the cold process, a very large amount of a resinous condensation product being always formed; a method of obtaining a satisfactory yield of betachloronaphthalene directly from the amido-compound has yet to be discovered.

80. "Methods of Observing the Spectra of Easily Volatile Metals and their Salts, and of Separating their Spectra from those of the Alkaline Earths." By W. N. HARTLEY, F.R.S.

The difficulty in obtaining persistent flame spectra of lithium, potassium, rubidium, caesium, and thallium has to some extent been surmounted by the contrivances designed by Mitscherlich, Gouy, and others, but as solutions are necessary, these methods have not been found satisfactory by the author.

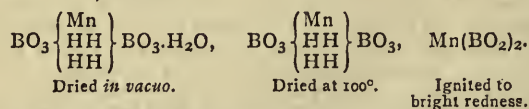
It is shown how flame colourations lasting for long periods may be obtained by converting the salts into fluosilicates, borates, or silicates. These compounds are less readily decomposed, and are more difficult to volatilise than the corresponding chlorides, sulphates, &c. Fused beads of the salts are held in the flame of a Bunsen burner on platinum wires, while measurements are made with the spectrometer.

When observing in the usual manner, the spectra of the alkalis are liable to be obscured by the presence of lines and bands due to the alkaline earths. By converting the material to be examined into a fluosilicate, borate, or silicate, the spectra of calcium, strontium, and barium are suppressed. If, however, the substance to be examined be converted into a borate, the alkali metals can first be observed, and subsequently by passing hydrogen chloride gas into the flame, the spectra of the alkaline earth metals become brilliantly visible. Although visible, the green bands due to boric oxide are feeble, and cause no confusion.

81. "Manganese Borate: its Constitution and Properties." By W. N. HARTLEY, F.R.S., and HUGH RAMAGE.

Particulars are given of the properties of manganese borate prepared in various ways from manganese sulphate and alkaline borates. Manganese borate dried *in vacuo*

over sulphuric acid is found to lose to the extent of 11.84 per cent of its weight water when heated at 100°; when heated from 100° to redness, it loses 19.65 per cent, which is water of constitution, the compound being a tetrahydric orthoborate, thus:—



By gradually heating the salt at fixed temperatures increasing to bright redness, and ascertaining the amount of water which it contained, a series of numbers was obtained from which a curve was drawn, the ordinate numbers being the percentages of water in the compound, and the abscissæ the corresponding temperatures. It was thus seen that there were five points above 100° at which dissociation was interrupted, and the compound in existence assumed a condition of stability. The following are the compounds of which the formation is inferred:—

Temp. of formation.	Formula of salt formed.	Water contained in compound.	
		Found.	Calculated.
22°	$\text{MnH}_4(\text{BO}_3)_2 \cdot \text{H}_2\text{O}$	26.86	27.69 per cent
100°	$\text{MnH}_4(\text{BO}_3)_2$	19.65	20.33 "
170°	$\text{MnH}_2\text{B}_2\text{O}_5$	11.45	11.32 "
195–220°	$\text{Mn}_{11}\text{H}_{20}\text{B}_{22}\text{O}_{54}$	10.43	10.40 "
255°	$\text{Mn}_6\text{H}_{10}\text{B}_{12}\text{O}_{29}$	9.71	9.61 "
295–305°	$\text{Mn}_3\text{H}_4\text{B}_6\text{O}_{14}$	7.20	7.84 "
Dull red heat	$\text{Mn}_4\text{H}_2\text{B}_8\text{O}_{17}$	2.87	3.09 "
Bright red	$\text{Mn}(\text{BO}_2)_2$	nil	
Partial fusion			

The solubility of manganese borate in various saline solutions was investigated; it was found to possess a maximum of solubility at or about 18°, and a minimum at 80°, so that when solutions are heated, they deposit the salt at this temperature.

It is believed that this is caused by the dehydration of the salt in solution, namely, $\text{MnH}_4(\text{BO}_3)_2 \cdot \text{H}_2\text{O}$, which becomes $\text{MnF}_4(\text{BO}_3)_2$, and this, being less soluble, is deposited: such a change being known to occur, and to be complete at 100° when the salt is heated in air.

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Address by ALBERT B. PRESCOTT, Retiring President,
Delivered at the Rochester Meeting, 1892.

THE IMMEDIATE WORK IN CHEMICAL SCIENCE.

A DIVISION of science has a work of its own to do, a work that might well be done for its own sake, and still more must be done in payment of what is due to the other divisions. Each section of our Association has its just task, and fidelity to this is an obligation to all the sections. Those engaged in any labour of science owe a debt to the world at large, and can be called to give an account of what they are doing, and what they have to do, that the truth may be shown on all sides.

If it be in my power to make the annual address of this meeting of any service at all to you who hear it—in your loyalty to the Association—I would bring before you some account of the work that is wanted in the science of chemistry. Of what the chemists have done in the past the arts of industry speak more plainly than the words of any address. Of what chemists may do in the future it would be quite in vain that I should venture to predict. But of the nature of the work that is waiting in the chemical world at the present time I desire to say what I can, and I desire to speak in the interests of science in general. The interests of science, I am well

assured, cannot be held indifferent to the interests of the public at large.

It is not a small task to find out how the matter of the universe is made. The task is hard, not because of the great quantity in which matter exists, nor by reason of the multiplicity of the kinds and compounds of matter, but rather from the obscurity under which the actual composition of matter is hidden from man. The physicists reach a conclusion that matter is an array of molecules, little things, not so large as a millionth of a millimetre in size, and the formation of these they leave to the work of the chemists. The smallest objects dealt with in science, their most distinct activities, become known only by the widest exercise of inductive reason.

The realm of chemical action, the world within the molecules of matter, the abode of the chemical atoms, is indeed a new world and but little known. The speculative atoms of the ancients, mere mechanical divisions, prefiguring the molecules of modern science, yet gave no sign of the chemical atoms of this century, nor any account of what happens in a chemical change. A new field of knowledge was opened in 1774 by the discovery of oxygen, and entered upon in 1804 by the publications of Dalton, a region more remote and more difficult of access than was the unknown continent toward which Christopher Columbus set his sails three centuries earlier. The world within molecules has been open for only a hundred years. The Sixteenth Century was not long enough for an exploration of the continent of America, and the Nineteenth has not been long enough for the undertaking of the chemists. When four centuries of search shall have been made in the world of chemical formation, then science should be ready to meet a congress of nations, to rejoice with the chemist upon the issue of his task.

It is well known that chemical labour has not been barren of returns. The products of chemical action, numbering thousands of thousands, have been sifted, and measured, and weighed. If you ask what happens in a common chemical change, you can obtain direct answers. When coal burns in the air, how much oxygen is used up can be stated with a degree of exactness true to the first decimal of mass, perhaps to the second, yet questionable in the third. How much carbonic acid is made can be told in weight and in volume with approaching exactness. How much heat this chemical action is worth, how much light, how much electromotive force, what train-load of cars it can carry, how long it can make certain wheels go round,—for these questions chemists and physicists are ready. With how many metals carbonic acid will unite, how many ethers it can make into carbonates, into what classes of molecules a certain larger fragment of carbonic acid can be formed, the incomplete records of these things already run through a great many volumes. These carboxylic bodies are open to productive studies, stimulated by various sorts of inquiry and demands of life. Such have been the gatherings of research. They have been slowly drawn into order, more slowly interpreted to meaning. The advances have been constant, deliberate, sometimes in doubt, always persisting, and gradually gaining firmer ground. So chemistry has reached the period of definition. Its guiding theory has come to be realised.

"The atomic theory" has more and more plainly appeared to be the central and vital truth of chemical science. As a working hypothesis, it has directed abstruse research through difficult ways to open accomplishment in vivid reality. As a system of knowledge, it has more than kept pace with the rate of invention. As a philosophy, it is in touch with profound truth in physics, in the mineral kingdom, and in the functions of living bodies. As a language it has been a necessity of man in dealing with chemical events. Something might have been done, no doubt, without it, had it been possible to keep it out of the chemical mind. But with a knowledge of the primary elements of matter, as held at the beginning of

this century, some theory of chemical atoms was inevitable. And whatever theory might have been adapted, its use in investigation would have drawn it with a certainty into the essential features of the theory now established. It states the constitution of matter in terms that stand for things as they are made. The mathematician may choose the ratio of numerical notation, whether the ratio of ten or some other. But the chemist must find existing ratios of atomic and molecular mass, with such degree of exactness as he can attain. Chemical notation, the index of the atomic system, is imperfect, as science is incomplete. However defective, it is the resultant of a multitude of facts. The atomic theory has come to be more than facile language, more than lucid classification, more than working hypothesis; it is the *definition of the known truth in the existence of matter*.

The chemical atom is known, however, for what it does, rather than for what it is. It is known as a centre of action, a factor of influence, an agent of power. It is identified by its responses, and measured by its energies. Concealed as it is, each atom has given proof of its own part in the structure of a molecule. Proofs of position, not in space, but in action, as related to other atoms, have been obtained by a multitude of workers with the greatest advantage. The arrangement of the atoms in space, however, is another and later question, not involved in the general studies of structure. But even this question has arisen upon its own chemical evidences, for certain bodies, so that "the configuration" of the molecule has become an object of active research.

Known for what it does, the atom is not clearly known for what it is. Chemists, at any rate, are concerned mainly with what can be made out of atoms, not with what atoms can be made of. Whatever they are, and by whatever force or motion it is that they unite with each other, we define them by their effects. Through their effects they are classified in the rank and file of the periodic system. The physicists, however, do not stop short of the philosophical study of the atom itself. As a vibratory body its movements have been under mathematical calculations; as a vortex ring its pulsations have been assumed to agree with its combining power. As an operating magnet its interaction with other like magnets has been predicated as the method of valence. There are, as I am directly assured, physicists of penetration and prudence now looking with confidence to studies of the magnetic relations of atoms to each other.* Moreover, another company of workers, the chemists of geometric isomerism, assume a configuration of the atoms in accord with that of the molecule.

The stimulating truth of the atomic constitution of the molecule, a great truth in elastic touch with all science, excites numerous hypotheses, which, however profitable they may be, are to be stoutly held at a distance from the truth itself. Such are the hypotheses of molecular aggregation into crystals and other mineral forms. Such are the biological theories of molecules polymerising into cells, and of vitality as a chemical property of the molecule. Such are the questions of the nature of atoms, and the genesis of the elements as they are now known, questions on the border of meta-physics. Let all these be held distinct from the primary law of the atomic constitution of simple molecules in gaseous bodies, an essential principle in an exact science. The chemist should have the comfortable assurance, every day, as he plies his balance of precision, that the atom-made molecules are there, in their several ratios of quantity, however many unsettled questions may lie around about them. Knowledge of molecular structure makes chemistry a science, nourishing to the reason, giving dominion over matter, for beneficence to life.

Every chemical pursuit receives strength from every advance in the knowledge of the molecule. And to this

knowledge, none the less, every chemical pursuit contributes. The analysis of a mineral, whether done for economic ends or not, may furnish a distinct contribution toward atomic valence. The further examination of steel in the cables of a suspension-bridge is liable to lead to unexpected evidence upon polymeric unions. Rothamsted farm, where ten years is not a long time for the holding of an experiment, yields to us a classic history of the behaviour of nitrogen,—a history from which we correct our theories. The analysis of butter for its substitutes has done something to set us right upon the structure of the glycerides. Clinical inspection of the functions of the living body finds a record of molecular transformations too difficult for the laboratory. The efforts of pharmaceutical manufacture stimulate new orders of chemical combination. The revision of the pharmacopœia every ten years points out a humiliating number of scattered errors in the published constants on which science depends. The duty of the engineer, in his scrutiny of the quality of lubricating oils, brings a more critical inquiry into the laws of molecular movement. There is not time to mention the many professions and pursuits of men who contribute toward the principles of chemistry and hold a share therein. If it be the part of pure science to find the law of action in nature, it is the part of applied science both to contribute facts, and to put theory to the larger proof. In the words of one who has placed industry in the greatness of its debts to philosophic research, W. H. Perkin, "There is no chasm between pure and applied science, they do not even stand side by side, but are linked together." So in all branches of chemistry, whether it be termed applied or not, the best workers are the most strongly bound as one, in their dependence upon what is known of the structure of the molecule.

Studies of structure were never before so inviting. In this direction and in that especial opportunities appear. Moreover, the actual worker here and there breaks into unexpected paths of promise. Certainly the sugar group is presenting to the chemist an open way from simple alcohols on through to the cell substances of the vegetable world. And nothing anywhere could be more suggestive than the extremely simple unions of nitrogen lately discovered. They are likely to elucidate linkings of this element in great classes of carbon compounds, all significant in general chemistry. Then certain comparative studies have new attractions. As halogens have been upon trial side by side with each other, so, for instance, silicon must be put through its paces with carbon, and phosphorus with nitrogen. Presently, also, the limits of molecular mass, in polymers and in unions with water, are to be nearer approached from the chemical side, as well as from the side of physics, in that attractive but perplexing border ground between affinity and the states of aggregation.

Such is the extent and such the diversity of chemical labour at present that every man must put limits to the range of his study. The members of a society or section of chemistry, coming together to hear each other's researches, are better able, for the most part, to listen for instruction than for criticism. Still less prepared for hasty judgment are those who do not come together in societies at all. Even men of eminent learning must omit large parts of the subject, if it be permitted to speak of chemistry as a single subject. These considerations admonish us to be liberal. When metallurgical chemistry cultivates scepticism as to the work upon atomic closed chains, it is a culture not the most liberal. When a devotee of organic synthesis puts a low value upon analytic work, he takes a very narrow view of chemical studies. When the chemist who is in educational service disparages investigations done in industrial service, he exercises a pitiful brevity of wisdom.

The pride of pure science is justified in this, that its truth is for the nurture of man. And the ambition of industrial art is honoured in this, its skill gives strength to man. It is the obligation of science to bring the

* "The results of molecular physics point unmistakably to the atom as a magnet, in its chemical activities."—A. E. Dolbear, in a personal communication.

resources of the earth, its vegetation and its animal life, into the full service of man, making the knowledge of creation a rich portion of his inheritance, in mind and estate, in reason and in conduct, for life present and life to come. To know creation is to be taught of God.

I have spoken of the century of beginning chemical labour, and have referred to the divisions and specialities of chemical study. What can I say of the means of uniting the earlier and later years of the past, as well as the separated pursuits of the present, in one mobile working force? Societies of science are among these means, and it becomes us to magnify their office. For them, however, all that we can do is worth more than all we can say. And there are other means even more effective than associations. Most necessary of all the means of unification in science is the use of its literature.

It is by published communication that the worker is enabled to begin, not where the first investigation began, but where the last one left off. The enthusiast who lacks the patience to consult books, presuming to start anew all by himself in science, has need to get on faster than Antoine L. Lavoisier did when he began, an associate of the French Academy in 1768. He of immortal memory, after fifteen eventful years of momentous labour, reached only such a combustion of hydrogen as makes a very simple class experiment at present. But, however, early in chemical discovery, Lavoisier availed himself of contemporaries. They found oxygen, he learned oxidation. One great man was not enough in 1774, both to reveal this element and show what part it takes in the formation of matter. The honour of Lavoisier is by no means the less that he used the results of others; it might have been the more had he given their results a more explicit mention. Men of the largest original power make the most of the results of other men. Discoverers do not neglect previous achievement however it may appear in biography. The masters of science are under the limitations of their age. Had Joseph Priestley lived in the seventeenth century he had not discovered oxygen. Had August Kekulé worked in the period of Berzelius, some other man would have set forth the closed chain of carbon combination, and Kekulé, we may be sure, would have done something else to clarify chemistry. Such being the limitations of the masters, what contributions can be expected in this age from a worker who is without the literature of his subject?

In many a town some solitary thinker is toiling intensely over some self-imposed problem, devoting to it such sincerity and strength as should be of real service, while still he obtains no recognition. Working without books, unaware of memoirs on the theme he loves, he tries the task of many with the strength of one. Such as he sometimes send communications to this association. An earnest worker, his utter isolation is quite enough to convert him into a crank. To every solitary investigator I should desire to say, get to a library of your subject, learn how to use its literature, and possess yourself of what there is on the theme of your choice, or else determine to give it up altogether. You may get on very well without college laboratories, you can survive it if unable to reach the meetings of men of learning, you can do without the counsel of an authority, but you can hardly be a contributor in science except you gain the use of its literature.

First in importance to the investigator are the original memoirs of previous investigators. The chemical determinations of the century have been reported by their authors in the periodicals. The serials of the years, the continuous living repositories of all chemistry, at once the oldest and the latest of its publications, these must be accessible to the worker who would add to this science. A library for research is voluminous, and portions of it are said to be scarce, nevertheless it ought to be largely supplied. The laboratory itself is not more important than the library of science. In the public libraries of our cities, in all colleges now being established, the original

literature of science ought to be planted. It is a wholesome literature, at once a stimulant and a corrective of that impulse to discovery that is frequent among the people of this country. That a good deal of it is in foreign languages is hardly a disadvantage; there ought to be some exercise for the modern tongues that even the public high schools are teaching. That the sets of standard journals are getting out of print is a somewhat infirm objection. They have no right to be out of print in these days, when they give us twenty pages of blanket newspaper at breakfast, and offer us Scott's novels in full for less than the cost of a day's entertainment. As for the limited editions of the old sets, until reproduced by new types, they may be multiplied through photographic methods. When there is a due demand for the original literature of chemistry, a demand in accord with the prospective need for its use, the supply will come, let us believe, more nearly within the means of those who require it than it now does.

(To be continued.)

NOTICES OF BOOKS.

Painters' Colours, Oils, and Varnishes. A Practical Manual. By GEORGE H. HURST, F.C.S., Member of the Society of Chemical Industry, &c. With numerous Illustrations. London: Charles Griffin and Co., Ltd., 1892. Small 8vo., pp. 461.

THE author of this work has most laudably and successfully sought to combine theory with practice. It is consequently neither a collection of recipes to be followed in blind confidence, and apt, under novel circumstances, to lead to disasters, nor yet a theoretical disquisition rich in proposals often inapplicable in practice. Mr. Hurst opens his work with an explanation of the different senses in which the term "colour" is often used. He compares the two theories of colours; the older, mainly developed by Brewster, accepting red, yellow, and blue as the three primary colours, and the new view of Young and Helmholtz which regards red, green, and violet as the primaries. Our author shows that the modern theory explains most accurately all the phenomena of colour as produced with the pure spectral rays, but that Brewster's theory is the more convenient if we come to work with pigments or dye-liquors never absolutely pure.

In the second chapter he proceeds to white pigments, beginning with white-lead, which, in spite of its objectionable properties, is still by far of all painters' colours the most largely used.

We do not find that the author fully defines the sense in which he uses the two terms "assay" and "analysis." We conclude that by the former he understands a search for impurities or adulterations, which may especially interfere with the use of the colour, and by the latter the full quantitative determination of all ingredients present.

In Chapter III. we are informed that Chinese vermilion is not made by the wet process commonly given, but by a dry method differing little from that employed in Europe. The superiority of the Chinese product is ascribed to the greater care taken by the Chinese in the manufacture. No decision is given as to the comparative beauty and permanence of vermilions made respectively by the wet and the dry processes.

Brilliant scarlet, otherwise known as "geranium red," is mercuric iodide. Though more beautiful than vermilion it is little used on account of its high price and its fugitive character. We have observed, however, that if obtained not by precipitation but by grinding the two ingredients together in the proper proportions, the pigment obtained is much more permanent. The act of combination is sometimes attended with a flash of light,

Hence caution might be requisite if this process came to be used on an industrial scale.

The directions for the manufacture and the use of the chrome yellows, oranges, and reds, are thoroughly practical. It is remarkable that the chrome yellows, known in the trade as "pure," contain lead sulphate produced by the presence of sodium sulphate or alum. The cheaper sorts contain china clay, baryta, or whiting.

A chrome colour which we do not find mentioned is stannic chromate, known as "pink colour." It has the colour of a light madder lake and is remarkably permanent. It seems to have been hitherto used exclusively in porcelain-painting. Much confusion has been produced by the multitudinous synonyms affixed to some of the chrome colours. Thus chrome-reds are known as Persian red, Derby red, American vermilion, Chinese red, Victoria red, &c. Some of these names are exceedingly objectionable.

A table here given as showing the composition of "pure" chrome colours is very interesting. A "pure primrose chrome" contains 36.5 per cent of lead sulphate and a "pure scarlet" 39.47 of white-lead. The ochres and siennas are very fully described. The ochre obtained from Shotover, in Oxfordshire, is the highest in quality. The order of the value of ochres, as judged by the prices which they command, is:—Oxford, 100; French, 33; Derbyshire and Welsh, 25; Irish and Devon, 20.

Field's "Mars pigments" are described as possessing no advantage over the natural ochres, &c., in brightness and permanence, whilst they have the disadvantage of being more expensive. Turner's yellow and Naples yellow are correctly described as nearly obsolete, whilst King's yellow is condemned as being strongly arsenical and therefore dangerous. We submit, indeed, that arsenical compounds should always be abandoned if any harmless product can be found to take their place. The origin of Indian yellow (purree) is correctly described. It is little used, as it is very fugitive.

Cadmium yellow receives the favourable opinion which it merits. The author states that he has not succeeded in obtaining the red modification of cadmium sulphide.

Among the Brunswick greens we must mention that most of the commercial samples are frauds, mere mixtures of chrome yellow and prussian blue, with barytes, gypsum, &c. The true Brunswick green, basic copper chloride, is now obsolete. Guignet's green is the best of the chrome greens, insoluble in acids and alkalies, and neither affecting other colours nor affected by them.

The arsenical greens are utterly to be condemned on account of their danger. Mention is here made as to the disputed character of emerald green, or Schweinfurth green, for which we may refer to the conflicting views of Dr. Jabez Hogg and of Prof. Galloway. It would seem that the effects of minute doses of arsenic, as in case of the air of rooms papered with arsenical hangings, depend to some extent on the idiosyncrasy of the inmates; but as we cannot foresee what may be the susceptibility of persons living or sleeping in such rooms, the only safety lies in the total renunciation of such pigments.

The lake colours are fully and satisfactorily described; both the old class, composed of a colouring-matter in combination with alumina, stannic oxide, &c., or the newer class, formed with the coal-tar colours. Many of the latter do not give good results as oil colours. With the exception, perhaps, of the alizarin compounds, the lakes of the coal-tar colours are not sufficiently permanent for the uses of the artist.

The chapter on the assay and analysis of pigments will prove most valuable, both to consumers and dealers, as will also the table showing the action of light on colours. The experiments, which were made by Captain Abney and Dr. W. J. Russell were extended over two years.

Space will not allow us to extend our survey of this useful book, but we feel bound to recommend it to all persons engaged in the arts concerned.

CORRESPONDENCE.

DISINFECTANTS—AN EXPLANATION.

To the Editor of the Chemical News.

SIR,—Dr. Klein's letter in the CHEMICAL NEWS, vol. lxxvi., p. 304, necessitates a reply from me. It contains inaccuracies in its reference to "aminol" (with what it says of periodate crystals I am in no way concerned) which, if not promptly corrected, would do me injury.

1. The samples of "aminol" solution (strength 1 in 5000) to which Dr. Klein refers were sent to a number of medical men who had kindly consented to give it a trial in their practice. The reports so far received, which will be published in due course, record conspicuous successes, not only for this solution, but also of various dilutions thereof—even to 1 in 20,000.

2. Dr. Klein himself operated with a solution of the strength of 1 in 6000 in four out of the five series comprised in his experiments, and amongst the results obtained with it his report mentions the following:—

In Series IV.: "On *Staphylococcus aureus*, which may be taken as the most resistant microbe amongst those associated with surgical and other external disease processes, the 'aminol' solution (1 in 6000) did produce an effect, though a limited one, after two hours already, and after twenty-four hours' exposure destroyed the microbes."

In Series I.: "'Aminol' solution (1 in 6000) kills the *Bacillus Diptheriæ* in two hours. This was confirmed in Series III."

3. The "aminol" solution of the strength of 1 in 600, of which Dr. Klein's letter conveys the erroneous impression that it was the only one tested by him, was employed only in the fifth series. His statement of the disinfecting power of this strength is partly incorrect, partly misleading.

a. After twenty-four hours' exposure the growth of *Anthrax* spores was reduced from 100 to 6. That these remaining 6 would also have been eliminated after a little longer exposure (say another hour) will hardly be doubted, and that with a still more concentrated solution (say 1 in 400) complete disinfection would probably have been accomplished in a much shorter time than twenty-four hours (say eight to twelve hours) is certainly not an unreasonable assumption; nor should the possible enhanced effect of repeated applications be left out of sight in this connection. But after all, the question whether, and in what time, any strength of solution of "aminol" succeeds in destroying cultures of *Anthrax* spores is of no importance in medical practice. Dr. Klein himself, in the "Summary and Conclusions" of his report, points out "that the spores of *Bacillus Anthracis* may be left out of consideration, as they do not occur in the living body, and in infection with *Anthrax* generally the bacilli are always in the spore-free state, both in the blood and in the tissues."

b. Much more serious is the statement in Dr. Klein's letter, to the effect "that *Anthrax* bacilli, *Staphylococcus aureus*, and others were destroyed, but only after prolonged exposure." Now the facts, as recorded in Dr. Klein's report, are:—The four species of microbes operated upon besides *Anthrax* spores, and the results obtained, were the following:—

Sporeless <i>Bacillus Anthracis</i> , 1, 2,	
8, 12, and 24 hours	No growth.
<i>Staphylococcus aureus</i> , 1 and 2 hrs.	Growth reduced one-half to one-third.
<i>Staphylococcus aureus</i> , 8, 12, and 24 hours	No growth.
<i>Bacillus Diptheriæ</i> , 1, 2, 8, 12, and 24 hours	No growth.
<i>Streptococcus Erysipelatis</i> , 1 and 2 hours	Growth reduced to one-half.
<i>Streptococcus Erysipelatis</i> , 8, 12, and 24 hours	No growth.

From the above it is evident that when Dr. Klein's letter was penned he had not at hand either his notes or a printed copy of his own report, which was published last year with his full approval,—I am, &c.,

HUGO WOLLHEIM.

101, Leadenhall Street, E.C.,
December 19, 1892.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—I was much interested in Mr. Davis's letter which appeared in the *CHEMICAL NEWS* (vol. lxvi., p. 304). I know where a committee of a large corporation gas works in the Midlands offered £78 per annum for a competent chemist—which chemist was, moreover, to be under a manager who admitted that he was entirely ignorant of chemistry. The hours of the chemist were not short, from 9 a.m. till such time as his superior left him, often till 9 p.m.

Such a chemist must be a very meek individual, must show the best of results obtainable or unobtainable, for woe betide him should he bring the management of his superior (!) into question as the result of his work.

Now, in my humble opinion, night schools have done much to lower the standard of the salary of chemists. A case I know well, that of a young man following his trade of picture-frame making in the daytime, has elementary lessons in chemistry, and an hour's practical work for 20 or 30 evenings in the year, passes a not very formidable examination, and thus equipped, goes forth, not to benefit his picture-frame making, but to pose as an analytical chemist; and to obtain a footing, he will accept, nay, is proud of, a wage of £50 per annum. He is employed probably by a man who knows less chemistry than he himself does.

Failure to pass the examination as a pharmacist also adds to the number of analytical chemists of a low type. I know of instances where men have so failed and then fallen back on analytical work, and I do not think they are few and far between.

Another cause of the low salaries paid to chemists is brought about by chemical manufacturers constantly having fresh relays of youths in their laboratories, whom they paid nothing or at most only a nominal salary; and when a young man becomes fairly competent in the particular branch he is engaged in, he asks for his services to be rewarded, then he is told he is no longer wanted; as a rule, he cannot find employment in the same line, and having had no experience of any other, he is obliged to take a low salary like the picture-framer.

Now what must a person do who has had a college training for several years—perhaps taken an University Degree, obtained a thorough insight into the theory and practice of chemistry and its allied branches—unless he, too, accept £70 per annum? Otherwise he cannot, and I daresay does not, find employment.

I think that it would be well to commence with the oreigner when forming an Union, but I fear that little can be done, as the very men who are the cause of the complaint would join such a society as Mr. Davis indicates.—I am, &c.,

J. B. C.

December 19, 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxv., No. 23, December 5, 1892.

The Chemical Study of Opium-Smoking.—Henri Moissan.—The author sums up his results as follows.

There are two distinct cases; that where nothing is smoked but chandoo of very good quality, and where the smoke merely introduces into the lungs a very small quantity of morphia and of agreeable perfumes, and secondly that where the dregs or falsified opium are smoked which are decomposed not below 300°, with the formation of poisonous compounds such as pyrrol acetone and hydropyridic bases. We may compare this double action to the alcoholism produced in the one case by the repeated ingestion of a small quantity of alcohol of good quality, and in the other to the miserable state of the victims of absinthe. Arm. Gautier remarked that the most poisonous products of tobacco when smoked are hydropyridic bases.

Remarks on M. Barthe's recent Paper on the Volumetric Determination of the Alkaloids.—P. C. Plugge.—The author claims priority as against M. Barthe.

The Interchange of Carbonic Acid and Oxygen between Plants and the Atmosphere.—Th. Schlösing, jun.—The proportion of the volume of CO₂ which has disappeared to that of the oxygen which has appeared by the action of plants during the six or eight weeks of their growth, was found much below unity. In the third experiment the proportion did not appreciably vary in the course of vegetation. There enters into the composition of the organic matter of an entire plant a weight of hydrogen greater than that which would form water with the oxygen of this substance. The plant of the third experiment has derived oxygen to form its organic substance, not alone from the water and from the oxygen, and the carbonic acid of the atmosphere, but also to a considerable extent from the oxygenous minerals of the salt. The green plant is a reduction apparatus.

Bulletin de la Société Chimique de Paris.

Vols. vii. and viii., No. 22.

This issue contains an account of the life and researches of Auguste Thomas Cahours, with a list of his published researches.

Congress on Chemical Nomenclature.—An account of the proceedings at the Geneva Conference, the particulars of which have been already published in the *CHEM. NEWS*.

Study of the Rate of Decomposition of the Diazo-Compounds.—J. Haussier and P. Th. Muller.—This memoir requires the accompanying diagram, figure, and tables.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.
Photographic, 8.

WEDNESDAY, 28th.—British Astronomical Association, 5.
THURSDAY, 29th.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

SATURDAY, 31st.—Royal Institution, 3. "Astronomy," by Sir Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

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THE CHEMICAL NEWS.

VOL. LXVI., No. 1727.

ON THE VELOCITY OF CROOKES'S CATHODE STREAM.*

By Lord KELVIN, P.R.S.

IN connection with his splendid discovery of the cathode stream (stream from the cathode in exhausted glass vessels subjected to electric force), Crookes found that when the whole of the stream, or a large part of the whole, is so directed as to fall on 2 or 3 sq. c.m. of the containing vessel, this part of the glass becomes rapidly heated up to many degrees, as much as 200° or 300° sometimes, above the temperature of the surroundings.

Let v be the velocity, in centimetres per second, of the cathode stream, and ρ the quantity of matter of all the molecules in 1 c.c. of it. Supposing that Crookes's experiments seem to prove to be not far from the truth, that their impact on the glass is like that of inelastic bodies, and that it spends all their translational energy in heating the glass. The energy thus spent, per square centimetre of surface struck, per second of time, is $\frac{1}{2}\rho v^2$; of which the equivalent in grm.-water-centigrade thermal units is approximately $\frac{1}{2}\rho v^2/42,000,000$. The initial rate at which this will warm the glass, in degrees centigrade per second, is—

$$\frac{\frac{1}{2}\rho v^2}{10^6 \times 42 \cdot 0a} \dots \dots (1),$$

where σ denotes the specific heat of the glass, and a the thickness of it at the place where the stream strikes it.

The limiting temperature to which this will raise the glass is—

$$\frac{1}{E} \times \frac{\frac{1}{2}\rho v^2}{42,000,000} \dots \dots (2),$$

where E denotes the sum of the emissivities of the two surfaces of the glass in the actual circumstances.

It is probable that ρ differs considerably from the average density of the residual air in the enclosure. Let us take, however, for a conceivably possible example, $\rho = 10^{-6}$, which is what the mean density of the enclosed air would be if the vessel were exhausted to 8×10^{-6} of the ordinary atmospheric density.

To complete the example, take—

$$v = 100,000 \text{ c.m. per sec.}$$

(being about twice the average velocity of the molecules of ordinary air at ordinary temperature); and take—

$$\rho a = \frac{1}{2} \text{ c.m.,}$$

as it might be for an ordinary glass vacuum bulb; and take—

$$E = \frac{1}{2000},$$

which may not be very far from the truth.

With these assumptions, we find, by (1) and (2) approximately, 1° per second for the initial rise, and 375° for the final temperature, which are not very unlike the results found in some of Crookes's experiments.

The pressure of the cathode stream of the velocity and density which we have assumed by way of example is ρv^2 , or 100 dynes per square centimetre, or about 100 m.grms. heaviness per square centimetre, which is ample for Crookes's wonderful mechanical results.

The very moderate velocity of 1 kilom. per second which we have assumed is much too small to show itself by the optical colour test. The fact that this test has been applied, and that no indication of velocity of the luminous molecules has been found, has, therefore, no validity as an objection against Crookes's doctrine of the cathode stream.

DESCRIPTION OF A NEW ELECTRIC FURNACE.

By HENRI MOISSAN.

THE discovery of the oxygen blast, by Henri Sainte-Claire Deville and Debray, rendered great services to chemistry. By means of this apparatus it has not only been easy to melt and refine platinum and to obtain new alloys, but also to extend and generalise a certain number of questions in mineral chemistry.

The temperature which may be reached with this apparatus fed with coal-gas and oxygen is about 2000°. We know that Deville and Debray found no substance except quicklime to resist this temperature.

Having had occasion in former researches to submit various substances to a temperature exceeding 2000°, I thought of utilising the heat yielded by the electric arc. After some trials I finally adopted the arrangement which I submit to the Academy, the only claim of which is its extreme simplicity.

This new furnace is formed of two bricks of quicklime, carefully cut and placed one above the other. The lower brick has a longitudinal groove which receives the two electrodes, and in the middle is a small cavity which serves as a crucible. This cavity may be more or less deep, and contains a layer, some centimetres in thickness, of the substance upon which the thermic energy of the arc is to act. Or we may also arrange a small crucible of charcoal containing the substance to be ignited. Or for the reduction of oxides and the subsequent fusion of the metals we use larger crucibles, and a cylindrical aperture made in the upper brick allows of throwing from time to time into the furnace small packets formed of a compressed mixture of oxide and of carbon. The furnace, therefore, receives merely a single arc, and the diameter of the carbons which serve as conductors will, of course, vary with the intensity of the current. After each experiment the ends of the carbons are entirely converted into graphite.

In our first researches we used a small Edison machine driven by a gas engine of four horse power. Most commonly the current traversing the furnace indicated 30 ampères and 55 volts. The temperature reached did not much exceed 2250°. In a second series of experiments we utilised the force produced by an eight horse-power gas-engine. The apparatus for measuring indicated 100 ampères and 45 volts. The temperature reached was about 2500°. Lastly, thanks to the kindness of M. Violle we were able to carry out our third series of experiments at the Conservatoire des Arts et Métiers. We had at our disposal a force of fifty horse-power, and the arc obtained under these conditions measured up to 450 ampères and 70 volts. The temperature was about 3000°. We are bound to address our thanks to M. Tresca, whose kind assistance proved very useful to us in this last series of experiments.

When employing high tension currents it is very useful to take certain precautions and to insulate the conductors with care. But even with currents of 30 ampères and 50 volts, such as those employed at the outset of these investigations, it is imperative not to expose the face to a prolonged action of the electric light, and always to protect the eyes with spectacles having very deep-coloured glasses. Electric sun-strokes were very frequent at the beginning of these researches; the irritation of the eyes produced by the arc may occasion very painful congestions.

The temperatures obtained in this series of experiments are only given approximately. But M. Violle, not content with furnishing the means to carry out this research, has kindly undertaken the special determination of those different temperatures by procedures which he will lay before the Academy at an early date.

When we became accustomed to the management of

* Read before the Royal Society, December 8, 1892.

this furnace we were able to produce a number of reactions which we will briefly summarise.

When the temperature is close upon 2500° , lime, strontia, and magnesia crystallise in a few minutes. If the temperature reaches 3000° , even the material of the furnace, quicklime, melts and flows like water. At the same temperature, carbon quickly reduces calcium oxide, and the metal is liberated in abundance. It readily combines with the carbons of the electrodes, forming a calcium carbide, liquid at a red heat, and easy to collect. Chromium sesquioxide and magnetic iron oxide melt rapidly at 2250° . Uranium sesquioxide if heated by itself is reduced to the state of black uranous oxide, forming long prisms. Uranium oxide, which cannot be reduced by charcoal at the highest temperatures of our furnaces, is quickly reduced at 3000° . In ten minutes it is easy to obtain an ingot of 120 grms. of uranium.

The oxides of nickel, cobalt, manganese, and chrome are reduced by charcoal at 2500° in a few moments. This is a fine experiment for a course of lectures, as it does not require more than from ten to fifteen minutes.

This method enables us easily to cause boron and silicon to react upon the metals and to obtain borides and silicides in very fine crystals. Lastly, it is easy under the above conditions to cause this elevated temperature to act upon a number of substances, simple and compound.

We are continuing this study, and shall soon communicate our further results to the Academy.—*Comptes Rendus*, cxv., p. 1031.

MODERN CHANGE IN THE CHARACTER OF A MINERAL WATER.

By W. P. MASON.

SOME years ago Prof. C. F. Chandler made an analysis of the water derived from the deep well situated at Round Lake, N.Y., a summer resort situated some fifteen miles south of Saratoga. At that time the well was 800 feet deep; the delivery, by pumping, good, and the quality of the water saline and very acceptable. It then analysed as follows, in grains per U.S. gallon:—

Sodium chloride	394.2943
Potassium chloride	9.4363
Sodium bromide	1.4716
Sodium iodide	1.3152
Sodium fluoride	trace
Lithium bicarbonate	2.7494
Sodium bicarbonate	48.9871
Magnesium bicarbonate	9.7846
Calcium bicarbonate	13.4457
Strontium bicarbonate	1.2038
Barium bicarbonate	0.5520
Iron bicarbonate	0.6344
Manganese bicarbonate	0.0768
Potassium sulphate	1.0275
Sodium phosphate	0.0228
Sodium baborate	trace
Alumina	0.0346
Silica	1.2247
Organic matter	trace

486.2608

Some time since the owners, for reasons known to themselves, undertook to increase the output by sinking the well still deeper. Accordingly the boring was carried to a depth of 1400 feet, and a tube was inserted the entire length. The water obtained at this lower level was completely different from that previously furnished by the well, and at the same time quantities of gas, sufficient to light the premises, escaped from the tube. My analyses of both water and gas are appended:—

(Water results in grains per U.S. gallon).

Sodium sulphate	0.8584
Sodium chloride	15.7588
Sodium bicarbonate	86.0079
Sodium hyposulphite	0.0119
Sodium hydrosulphide	0.2345
Potassium sulphate	traces
Silica	0.3922
Oxide of iron and alumina	0.0619
Lithium bicarbonate	1.1313
Calcium carbonate	1.0966
Magnesium carbonate	0.9136

106.4671

The evolved gas consisted of—

	P.c. by volume.
Hydrogen sulphide	0.1
Oxygen	0.8
Carbon monoxide	0.3
Nitrogen	3.7
Methane	95.1

100.0

Rensselaer Polytechnic Institute,
Troy, N.Y.

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

(Concluded from p. 307).

THE double salt precipitated at the third treatment contained 1.240 grms. earth, having the equivalent $RO=119.83$, which in the state of nitrate showed the absorption lines of samarium very faintly. The gadolinia which remained in solution on the treatments I., II., and III., in the state of nitrate as a syrupy solution of the depth of 0.1 metre, gave only slight indications of samarium; there was not a trace present of other absorption lines. The close agreement of the equivalent of the three fractions, as well as the approximately accordant solubility of the gadolinium-potassium sulphate in a saturated solution of potassium sulphate, allow us to infer the unity and the purity of the three fractions. This assumption is confirmed by the circumstance that a portion of the earth weighing 1.57 grms. obtained from a mixture of the three fractions by partially precipitating the nitrate with dilute ammonia, gave the equivalent $RO=120.19$. As the mean value obtained for gadolinia we should have the equivalent $RO=120.18$, $R_2O_3=360.54$, whence the resulting atomic weight of gadolinium is $R=104.22$, III $R=156.33$. Gadolinia, if strongly ignited, is nearly white powder with a slight yellowish cast. It is easily dissolved by acids, and yields perfectly colourless salts. If slightly heated in a current of hydrogen it becomes perfectly white without any change of weight. If very intensely ignited in the same current it seems to undergo a partial reduction, as it takes a very tender, grey cast, with a slight loss of weight of 0.11 per cent. This grey cast disappears again on heating in a current of air. 1.1874 grms. gadolinia, after intense ignition in a porcelain tube filled with hydrogen, weighed only 1.1860 grms.

After heating in a current of air the original weight was again obtained. If the grey earth is treated with very dilute hydrochloric acid, avoiding any rise of temperature, there is left a small residue of a dark colour. The earth which has passed into solution, if separated by oxalic acid and ignited, on renewed treatment with hydrogen becomes again a light grey. By frequent repetition we may obtain a rather larger quantity of this grey

* From Liebig's Annalen.

substance. On ignition in air it yields gadolinia of the same colour and the same equivalent as the material originally used for the experiment. 0.6281 grm. oxide yielded 1.0454 sulphate, $RO=120.20$.

Gadolinia, if heated in air to bright redness, exhibits in a vacuum intense fiery red cathodic luminescence. Its spectrum consists of an orange-red line, very bright and sharp, the middle of which falls at the wave-length $\mu\mu$ 6094. It is well suited for the recognition of gadolinia. There are also indications of bands which, however, on account of their extremely feeble illumination, admit only of approximate measurements. I give them in the following conspectus:—

$\lambda = \mu\mu$ 6282.	Middle of an extremely faint band.
" " 6094.	Middle of an intensely bright, narrow, orange-red band.
" " 5925.	Indication of a narrow band.
" " 5860.	" " "
" " 5800.	" " "
" " 5745.	Beginning of an extremely faint band, which gradually vanishes.
" " 5502.	Indication of a narrow band.
" " 5420.	" " "
" " 5320.	" " "

From here onwards the spectrum becomes continuous, decreasing in intensity, and vanishes at $\lambda = \mu\mu$ 4810.

The luminescence band, $\lambda = \mu\mu$ 6094, has been previously observed by W. Crookes in a mixture of yttria and samaria. He characterised it then as an anomalous line, and believed it must be attributed to samaria. Subsequent experiments showed him that samaria prepared from gadolinite did not show this band, and that it appears only in those earths of samarskite which immediately follow samaria on a systematic decomposition by fractionated precipitation with ammonia. W. Crookes now ascribed this band to a new element in samarskite. Previously he had described a luminescence spectrum of the then unknown earth Ya (gadolinia), and given a drawing of it, in which, along with other sharper and brighter bands, the line 6094 was laid down. He regards the bands $\lambda = \mu\mu$ 5410 and 5450 as characteristic of gadolinia.

On the spark spectrum of gadolinium chloride we have only a communication by Lecoq de Boisbaudran. He describes it as composed of a great number of faint bands with separate bright lines, and gives precise measurements of their wave-lengths. I have never been able to obtain this spark spectrum, although I, finding myself thus disagreeing with so prominent and experienced a spectroscopist, spared neither time nor trouble. My gadolinia, $RO=120.18$, as a chlorine compound gives neither lines nor bands, whether in concentrated or dilute aqueous solutions, at the most different spark-lengths of a very powerful spark-inductor. At a distance of about 3 m.m. of carbons saturated with the concentrated chlorides there sometimes appear in the green part of the spectrum indications of single lines, but careful measurements proved that they were due to traces of samaria, which I had not been able to eliminate from my preparation of gadolinite earths.

THE ANALYSIS OF FERROCHROME, FERRO-ALUMINIUM, FERROTUNGSTEN, FERROSILICON, AND FERROTITANIUM.*

By A. ZIEGLER.

(Concluded from p. 295).

The opening up of ferroaluminium and the determination of the accompanying elements is effected essentially in the same manner as that described for ferrochrome. The quantity of the sifted material used is from $\frac{1}{2}$ to 1 grm.

* From the *Zeit. Anal. Chemie*.

Ferroaluminium, in consequence of its larger proportion of iron, requires rather more prolonged fusion than ferrochrome. It is advantageous to apply heat whilst dissolving the melt in water. Of course, with ferroaluminium no carbonic acid is introduced after the melt is dissolved, and the solution is not evaporated to dryness lest the sodium aluminate formed should be decomposed. On the contrary, it is well to add a little alkaline hydroxide whilst dissolving. On dissolving the residue of the melt in hydrochloric acid after extraction in water, any portions which have not been opened up require particular attention. The first separation of the aluminium from the bulk of the alkalies in the filtrate of the solution of the melt can also be very well effected without the introduction of carbonic acid by an accurate neutralisation with hydrochloric acid and the application of heat.

Ziegler recommends likewise the following method for the analysis of ferroaluminium. He dissolves $\frac{1}{2}$ grm. of the substance in powder or borings in the quantity of hydrochloric acid (1:3) required for solution in a platinum capsule (1), evaporates to dryness, melts with an excess of sodium carbonate or potash-soda, and proceeds with the aqueous solution of the melt for the determination of the aluminium after the separation of the silica substantially as described for the determination of chrome. But we may also, as it is preferable, introduce the desiccated hydrochloric solution into the silver crucible by means of a moistened filter, free from ash, and effect here the separation completely by fusion with six parts sodium hydroxide and three parts soda-saltpetre.

In other respects we proceed as directed for the analysis of ferrochrome.

If iron is still present in the precipitate of alumina, which may be perceived by its yellowish colour, after ignition it may be dissolved by fusion with bisulphate free from iron; the iron after reduction may be titrated with zinc, free from iron, and deducted as ferric oxide. Aluminium may also be freed from any trace of iron by repeated fusion with soda. Ferrotungsten may be likewise opened up by fusion with caustic alkali and an alkaline nitrate in a silver crucible, and in the further analysis all the points laid down under ferrochrome must be observed.

The proposed flux is also suitable for opening up ferrosilicon. But ferrosilicon may be quite as well decomposed by fusion with sodium bisulphate in a platinum crucible. The silica remaining after treatment with water is filtered off, and after weighing volatilised with hydrofluoric and sulphuric acids. This latter method, according to Ziegler, can be considered unobjectionable only if it is established that during this process no trace of silicon is lost as silicon hydride.

Ferrotitanium cannot be sufficiently decomposed with the flux above mentioned. The following method yields results which are technically satisfactory. One-half grm. of the alloy, pulverised and sifted, are opened up with sodium bisulphate exactly in the same manner as directed for ferrochrome, but the melt is dissolved in cold water. The residue, if no undecomposed substance is present (in which case the fusion must be repeated) must be evaporated off with hydrofluoric and sulphuric acids, whereby the silica is determined. Any essential residue is once more opened up with sodium bisulphate and added to the main solution. This is now diluted to about 1 litre, neutralised with ammonia, and mixed with an aqueous solution of sulphurous acid. It is then slowly heated to ebullition and boiled (covered), replacing the evaporated water if needed for one and a half to two hours.

If we operate in this manner almost all the iron remains in solution as a ferrous salt at the first precipitation. The precipitate is filtered, if necessary, through a double filter and washed with acetic acid at about 4 per cent. The filtrate must be absolutely clear. It is then nearly neutralised with ammonia, mixed with aqueous sulphurous acid, and boiled for an hour as a check on complete precipitation.

The first precipitate of hydrated metatitanic acid (still

containing iron), is evaporated to dryness, opened up with bisulphate, and treated in the same manner as the solution from the first opening up. If the operation is properly conducted the second precipitation gives a pure white precipitate of titanous acid containing mere traces of iron. If iron is present in a larger quantity, the opening up and precipitation are repeated. The precipitate thus obtained after incineration, treatment with ammonium carbonate, and sufficient ignition is pale, greyish brown titanous acid, which, on ignition, appears deep lemon-yellow, almost orange.

In the determination of titanous acid the author calls attention to the following points. If the liquid passes the filter in a turbid state, the addition of ammonium chloride is beneficial; or the precipitate may be mixed up with the paper of a filter containing a known proportion of ash. Hydrated titanous acid retains sulphuric acid obstinately, whence the incinerated precipitate must be cautiously heated with ammonium carbonate.

Half a gram. ferrotitanium is decomposed in about two hours on gentle heating with aqueous hydrofluoric acid. Melting soda-salt-petre does not take up any titanium from ferrotitanium. This alloy is imperfectly decomposed by hydrochloric, nitric acid, and *aqua regia*.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1892.

By WILLIAM CROOKES, F.R.S.,

and
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, December 7th, 1892.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 181 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from November 1st to November 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

As pointed out by anticipation in our report for September, the lowness of the average proportion of organic matter present in the Metropolitan water supply for many months past could not, with the abundant fall of the leaf, and greater or less stagnation of fluvial vegetation attendant on the coming on of winter, be expected to be much longer maintained. It was indeed well maintained during the month of October, but in the case of the supplies furnished by each of the seven Companies during the past month of November, there was a noticeable increase in the proportion of organic matter present in the water, as indicated alike by the estimations of organic carbon, of oxygen required for oxidation, and of degree of colour tint.

In the case of the Thames-derived water, for example, the mean amount of organic carbon in the supply for the month was found to be 0.204 part, and the maximum amount in any single sample examined 0.285 part in

100,000 parts of the water, as against a mean of 0.117 part, and a maximum of 0.155 part per 100,000 parts of water in the previous six months' supply, the mean increase, though relatively large, amounting indeed to an absolute addition of only 0.087 part of organic carbon in 100,000 parts of the water, corresponding as nearly as may be to an addition of about one-sixth of a grain of organic matter per gallon.

The vegetable origin, moreover, of this small additional amount of organic matter is inferable from the fact that, while the mean ratio of carbon to nitrogen in the minute proportion of organic matter present in the supply during the previous six months was as 100 : 27.1, the mean ratio in the larger proportion present in the November supply was as 100 : 19.8; or, inferentially, the ratio of carbon to nitrogen in the excess of organic matter present in the November supply was as 100 : 9.4 only.

Of the 182 samples of water examined by us during the past month, the entire number were found to be well-filtered, clear, and bright. The flooded state of the rivers at the beginning of the month, consequent on the heavy rainfall during the last days of October, was altogether without noticeable effect on the character of the water supply. Throughout November there was no heavy rainfall, and the total fall was slightly below the average.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

OBSERVATIONS ON FERRO-TUNGSTEN.*

By WM. H. WAHL.

IN the course of an investigation carried on during the past two years by the writer, in conjunction with Dr. William H. Greene, with the object in view of producing pure ferro-alloys, we made a number of experiments with ferro-tungsten.

These tungsten alloys exhibited similar physical properties, possessing considerable hardness and toughness, an extremely fine crystalline texture, with a fracture resembling that of tool-steel, and a specific gravity ranging between 9.3 and 10.14.

Some of the fractures, however, exhibited the fact that the alloy was not entirely homogeneous, disclosing under the glass and in places to the eye the presence of what are apparently smooth cleavages of imperfect crystals scattered through the finely-crystalline matrix of the alloy. The specimen shown you will illustrate my statement.

A sample of the alloy of 10.14 specific gravity was analysed at my suggestion by Mr. J. F. de Benneville in the laboratory of Dr. Gent. The result of the analysis exhibited a very high percentage of tungsten in the sample, and its behaviour towards liquid and fused solvents proved the interesting fact that a large proportion of the tungsten was present in the uncombined condition, as metallic tungsten, crystallised in the matrix of the alloy. The facts upon which Mr. de Benneville has founded this observation will appear in the following extract from a letter describing briefly the method pursued in his analytical work:—

"*Aqua regia* attacked it, although not energetically, and by decanting and adding fresh portions of acid from time to time a residue was obtained which resisted further action by acids, or by fusion with Na_2CO_3 and KNO_3 . It was a heavy, black, pulverulent substance, and in its negative action towards solvents answered to tungsten, which I took it to be. It gave 22.54 per cent of the original material. A second portion of the material

* Read at the Meeting of the Chemical Section of the Franklin Institute, November 15, 1892.

(powdered in a steel mortar) was fused with a mixture of Na_2CO_3 and KNO_3 , lixiviated, and the residue weighed. This was fused again and the residue weighed, the second weighing being practically the same, and yielding 22.80 per cent of the original material. Using strong HCl (1.20 sp. gr.) in successive portions, decanting, igniting the residue, and treating again with acid, gave me 21.74 per cent."

The foregoing extract appears fully to justify the conclusion that the undissolved residue represents the metallic tungsten present in the alloy in the uncombined state.

The composition of the metal analysed by Mr. de Benneville is as follows:—

	Per cent.
C	0.85
P	0.041
Si	0.14
Mn	trace
Fe	42.28
W (metal)	22.54
W (alloy)	34.35

100.201

A study of these figures reveals another interesting fact to which I desire to call your attention.

Taking the figures of the iron and combined tungsten (42.28 : 34.35) and calculating the percentage of tungsten which this ratio represents, we obtain 44.82 per cent tungsten. A calculation shows also that the figures representing the compound Fe_4W are almost identical with the ratio above named, to wit:—

Fe_4W found. Per cent.		Fe_4W by theory. Per cent.		Difference.
Fe	55.18	Fe	54.91	—0.27
W	44.82	W	45.09	
100.00		100.00		

The conclusion would seem to be justified by the facts above noted, that the saturation point of iron for tungsten is represented by the ratio exhibited in the compound Fe_4W , and that any excess of tungsten, above this ratio, present in a tungsten iron will remain uncombined.

I wish to express this statement as *probably* the correct interpretation of the facts, for it is hazardous to make a generalisation of this kind on the results of a single analysis.

It may be interesting to note in conclusion that Howe, in his "Metallurgy of Steel," refers to several cases of ferro-tungsten indicating the composition Fe_5W , and that the works on metallurgy as a rule accept without question the dictum that iron and tungsten will unite in all proportions. In the light of the facts given in this paper, this last statement requires qualification.

THE ELECTROLYSIS OF METALLIC FORMATES.*

By HILL SLOANE WARWICK.

(Concluded from p. 311).

Cadmium from Cobalt.

Cadmium taken.	Cobalt taken.	Cadmium found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.0984	0.1080	—	25	100	0.5	22	—
2. 0.0984	0.1080	—	25	150	0.8	45	—
3. 0.0984	0.1080	—	50	150	1.5	18	—

* Read before the American Philosophical Society, November 6, 1891. From the *Proceedings of the American Philosophical Society*, xxxi., No. 136.

It was naturally expected that cadmium would be completely precipitated from cobalt and nickel by employing a weak current, but from an examination of the above results it will be seen that a separation was not accomplished.

Even with a current of 1.5 c.c. OH gas per minute, the cadmium failed to deposit completely and was contaminated with cobalt (3). It was very spongy, and the solution still contained cadmium at the expiration of twenty-two hours. The current was then increased and allowed to act for forty-five hours (2). Cadmium was found in the solution, cobalt in the deposit. The distance between the electrodes was 2.8 c.m.

Cadmium from Nickel.

Cadmium taken.	Nickel taken.	Cadmium found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.0984	0.1028	0.0758	35	150	0.5	19	—
2. 0.0984	0.1028	0.1045	35	150	1.5	21	—
3. 0.0984	0.1028	0.1348	50	125	1.5	17	—

The results were quite as unsatisfactory as with cobalt. Cadmium was found in all three solutions, and more or less nickel was found in the deposits. In 3 the nickel came out as a grey deposit on the cadmium. The deposit was firm and adherent, although dark in colour. The distance between the electrodes was 2.5 c.m., except 3, in which the pole separation was 2.8 c.m.

Zinc from Cobalt.

Zinc present.	Cobalt present.	Zinc found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
1. 0.1006	0.1080	—	50	175	3	17	—
2. 0.1006	0.1080	—	100	175	5	18	—

Zinc from Nickel.

Zinc present.	Nickel present.	Zinc found.	Free acid.	H_2O .	OH gas per min.	Time.	Diff. from theory.
Grm.	Grm.	Grm.	C.c.	C.c.	C.c.	Hrs.	Perct.
3. 0.1006	0.1028	—	50	175	2.7	18	—
4. 0.1006	0.1028	—	100	175	5	18	—

2 and 4 were performed under similar conditions. The distance between the poles was 2.2 c.m. The current was generated by a battery of Bunsen cells. Even with a current of 5 c.c. gas per minute zinc was found in the solution in traces, while considerable quantities of cobalt and nickel separated as a coating upon the cadmium. 1 and 3 were also failures. A separation was not obtained even approximately.

Summary.

As a result of the foregoing experiments, it was found that the amount of copper, cadmium, or zinc deposited in a given time was proportional to the strength of the solution, and that the presence of free acid in moderate quantity did not materially affect the result.

Increasing the distance between the poles resulted in diminishing the amount of metal deposited, but the rate of decrease diminished as the distance between the electrodes increased.

Elevation of temperature caused an increase in the amount of metal deposited, the rate of increase being greatest at 80° in neutral and acid copper solutions, and at 60° in cadmium solutions containing free acid. On the other hand, the amount of zinc deposited in solutions to which free acid had been added diminished as the temperature rose, nothing being deposited at 80°.

Attempts to secure compact and adherent deposits of cadmium and zinc in neutral solutions were failures.

In acid solution copper and cadmium separated completely and satisfactorily. The zinc deposits were spongy, but the precipitation was complete.

Lead was mainly deposited on the negative pole, both in neutral and acid solutions. Manganese was precipitated on both poles, but the amount of peroxide separating on the cathode was reduced to mere traces by the presence of free acid.

The following separations were satisfactorily accomplished:—Copper from zinc, cobalt, and nickel, and cadmium from zinc and manganese.

Attempts to deposit copper in the presence of iron and cadmium, and zinc in the presence of iron, cobalt, and nickel, were successful. Nor was it possible in the presence of the last three metals named to estimate cadmium.

In conclusion I wish to express my obligations to Prof. Edgar F. Smith, at whose suggestion the work was undertaken. To his supervision and advice is largely due whatever value may attach to these results.

A RAPID METHOD FOR PHOSPHORUS DETERMINATION IN IRON, STEEL, AND ORES.*

By JAMES O. HANDY,
Chemist of the Pittsburgh Testing Laboratory.

No method of determining phosphorus will find favour among chemists unless it possesses advantages over existing methods. While retaining the accuracy of the best methods now known, it must be simpler, more rapidly executed, or less expensive. My belief that the process which I have worked out is a step in this direction is my reason for now describing it.

I owe to Mr. C. E. Manby's paper, in the *J. A. and A. C.* for February, 1892, the suggestion of essential points in my process. The method which he gives is too long, and would not compete with the Emmerton-Drown-Jones method (*A. I. M. E.*, February, 1890), which can be executed, with proper appliances, in thirty minutes, or less. Mr. E. F. Wood's latest method, a gravimetric one, is said to yield results in twenty minutes. I do not know how uniformly reliable these results are. I believe that they are always checked by a longer method.

I have proved by a great many experiments that several of the steps of Mr. Manby's process can either be safely dropped or simply modified, and a rapid and satisfactory process produced.

My method consists of the following points:—

(a). Separation of the phosphorus as pure phosphomolybdate of ammonium by washing with neutral potassium nitrate solution after the regular washing with 1 per cent nitric acid.

(b). Solution of the pure phospho-molybdate in a measured volume of a standard sodium hydrate solution. A definite quantity of the alkali is taken up in neutralising the phospho-molybdate.

(c). Titration of the excess of sodium hydrate by means of standard nitric acid. Phenol phthalein is used as the indicator. The end reaction is very distinct. Duplicate analyses give closely concordant results, which agree exactly with determinations of phosphorus by gravimetric methods. Without any special appliances, and without use of suction, an analysis can easily be done in thirty minutes. I am confident that this time can be shortened one-half. An analysis has in fact just been done in seventeen minutes. (March 29th).

The first part of the process is essentially that of Dr. Drown (*A. I. M. E.*, June, 1889). I have confirmed, by long experience, Dr. Drown's statement that sugar can be safely used as a reducing agent in the process. Clemens Jones substituted ferrous sulphate, but I find that it requires several times as much ferrous sulphate

as sugar for reduction, and that the sugar produces no ill effects. Pure granulated sugar is used.

The Method.

Dissolve 2 grms. of steel in a 12-ounce Erlenmeyer flask in 75 c.c. of nitric acid (1.13). To the boiling solution add 15 c.c. of permanganate solution (5 grms. per litre). Boil until pink colour disappears. Oxidation of the carbon and phosphorus is complete if there remains a brown precipitate of oxide of manganese. More permanganate will be required only in the analysis of iron or steel of very high carbon. Remove flask for a moment from the light. Add about $\frac{1}{10}$ gm. of granulated sugar. Replace flask on the light, and heat till the solution clears. Take flask off the light, and, after two or three minutes, add 13 c.c. of 0.09 ammonia. If the latter is poured carefully down the side of the flask, no loss by spattering will occur. Agitate the flask contents till, in a moment, the ferric hydrate is re-dissolved. Insert thermometer, and cool (or warm) to 85° C. Add 50 c.c. of molybdate solution, causing it to rinse off the thermometer as it flows into the flask. Insert rubber stopper. Wrap flask in towel, or put it into a shaking box, and shake it for five minutes. Filter immediately, using a 9 c.m. Swedish filter, and moderate suction. The precipitation is complete, and the precipitate shows no tendency to run through the filter. Wash out flask, and wash the filter and contents five times with 1 per cent nitric acid; wash five times with $\frac{1}{10}$ per cent potassium nitrate wash (1 gm. per litre). Place filter and contents in the flask. Add from a pipette 10 or 20 c.c. of standard sodium hydrate solution. Shake for a moment until the yellow precipitate is dissolved. Dilute with water to about 50 c.c. Add three drops phenolphthalein solution and titrate with standard nitric acid till the pink colour disappears. The cubic centimetres of standard sodium hydrate used up in neutralising the yellow precipitate represent the hundredths per cent of phosphorus in the sample analysed.

Reagents.

Molybdate Solution.—E. F. Wood's 1888 formula.—One pound of molybdic acid is mixed with 1200 c.c. of water in a stone-ware jar; 700 c.c. of ammonia (0.90 sp. gr.) are stirred in, and the stirring continued till all soluble matter is dissolved. 300 c.c. of conc. nitric acid (sp. gr. 1.42) are added to partially neutralise the ammonia in the solution. In each of four 2½ litre bottles is placed a mixture of 500 c.c. nitric acid (sp. gr. 1.42) and 1200 c.c. of water.

Pour 550 c.c. of the molybdate solution through a funnel into each bottle, and mix the contents by a slight rotating motion. If the stream of molybdate solution flows quickly and continuously into the acid mixture, no separation of molybdic acid takes place. Both solutions may be hot when mixed.

I have used this formula for three years with uniform success, and have seen it in continuous use in many other laboratories. Little or no separation of molybdic acid takes place on standing, but we always filter it just before using.

Filter Paper.

No. 1 "F." Munktel's Swedish filter paper has given us entire satisfaction. We are much pleased with its uniformity.

Nine c.m. filters are used.

Pure Yellow Precipitate.

This can be prepared from acidified ammonium or sodium phosphate by precipitating with molybdate solution. Wash the precipitate with 1 per cent nitric wash. Dry at 100° C. Keep in glass-stoppered bottles for use.

Use (one-tenth gm.) for standardising the sodium hydrate solution for work on steels, &c., containing from 0.050 to 0.150 per cent of phosphorus. For high phosphorus work use a quantity of phospho-molybdate

* Chemical Section of the Engineers' Society of Western Pennsylvania.

approximately equal to the amount obtained from the analysis of two grms. of the metal. This precaution avoids multiplying the slight excess of nitric acid which is added when titrating excess of sodium hydrate. This excess would be one drop or perhaps one-tenth c.c., and would become significant if multiplied by five or ten. By observing this precaution the accuracy of the method may be preserved through a wide range of phosphorus percentage.

When the method is once established in a laboratory the standardisation of the sodium hydrate solution may be more conveniently done by means of steel or pig-iron of known phosphorus contents.

Standard Sodium Hydrate.

15.4 grms. of sodium hydrate are dissolved in 100 c.c. of water. Saturated barium hydrate solution is stirred into the sodium hydrate solution until no more precipitation occurs. Filter at once and make up to two litres with distilled water. In practice I shall make up 154 grms. of sodium hydrate at once, freeing it from carbonate as above and make up 2 litres. 200 c.c. of this made up to 2 litres will make the standard approximately.

Standard Nitric Acid.

For a stock solution make up 200 c.c. of nitric acid (sp. gr. 1.42) to 2 litres. 200 c.c. of the stock solution is made up to 2 litres for approximate standard. Run the standard alkali and acid against each other, and having ascertained their relative strengths, add sufficient water to the stronger of the two to make the solutions equal in value.

Next run the sodium hydrate solution against 0.1000 gm. pure ammonium phospho-molybdate = 0.00163 gm. phosphorus. If its strength is too great (e.g., if 1 c.c. = 0.000206 gm. phosphorus) add to two litres of the standard sodium hydrate 60 c.c. of water. In order to preserve the equality of the acid and alkali solutions, add to two litres of the standard nitric acid 60 c.c. of water and mix. The solutions will then be equal, and 1 c.c. = 0.0002 gm. of phosphorus or $\frac{1}{5000}$ per cent phosphorus, when 2 grms. of the sample are taken for analysis.

Phenolphthalein Indicator.

Five-tenths gm. of phenolphthalein are dissolved in 200 c.c. of 95 per cent alcohol. Use about 3 drops for each titration.

We feel sure the phospho-molybdate of ammonium, as we obtain it in this process, contains, when dried at 100° C., 1.63 per cent of phosphorus. Our reasons are as follows:—

1. Mr. E. F. Wood finds 1.63 per cent phosphorus in the phospho-molybdate obtained by his method and dried at 100° C. (See *J. A. C.*, 1888).

2. We have found by hundreds of analyses the absolute agreement of results by Mr. Wood's process with those by Dr. Drown's (*A. I. M. E.*, 1889) process, modified by weighing instead of titrating the yellow precipitate.

3. Dr. Franz Hundeshagen, in a very elaborate series of researches (*Z. A. C.*, 1889), finds that phospho-molybdate precipitated and purified, as we do it, has 1.63 per cent of phosphorus when dried at 150° C.

4. We find that pure phospho-molybdate dried at 100° C. suffers no further loss of weight when dried at 150° C. Hence we have two authorities to prove that the phospho-molybdate as we obtain it contains 1.63 per cent phosphorus.

5. We find that results obtained by precipitation at temperatures from 20° to 85° C. are identical.

6. We find that samples precipitated at 85° C. can be filtered immediately and correct results obtained, while at lower temperatures longer standing is needed before precipitation of the phosphorus is complete.

7. We find by experiments on a sample of steel containing 0.014 per cent of arsenic that the phosphorus can

be correctly estimated by our method without added precaution.

8. We find perfect agreement between results by weighing the yellow precipitate and results by titrating the same by our method.

Tables of results of some of the experiments by which we established the accuracy of the method are given below:—

No.	Results by weighing phospho-molybdate.		Results by titrating phosphomolybdate.	
	Per cent phosphorus.		Per cent phosphorus.	
4289	..	..	0.093	0.093
4290	..	..	0.089	0.088
4291	..	..	0.096	0.095
4292	..	..	0.038	0.039
3143	..	..	0.037	0.038
A ..	..	..	0.090	0.089
3211	..	..	0.088	0.087
3212	..	..	0.090	0.089
3214	..	..	0.033	0.033
3213	..	..	0.089	0.091
3216	..	..	0.088	0.087
4288	..	..	0.071	0.072
152	..	..	0.425	0.422
4327	..	..	0.030	0.030
Blair	..	..	0.098	0.098
	..	..	0.097	
	..	..	0.097	

The last sample contains, according to Messrs. Booth, Garrett, and Blair, phosphorus 0.097 per cent, arsenic 0.014 per cent.

DISCUSSION.

Mr. MANBY—I am very glad indeed to see that my method has been so quickly taken up and improved by Mr. Handy, and that he has obtained such good results with it. I hope that the investigations of your committee will confirm his results. I have made estimations with the method in forty minutes, and I am pleased to see that this time has been cut down one-half by Mr. Handy. I found that the presence of ammonia salts was prejudicial to the accuracy of the titration, and I therefore resorted to the process of purifying the yellow precipitate by igniting it moderately over a lamp to expel ammonium nitrate. I consider the freeing of the yellow precipitate from acid and ammonium salts, by washing with $\frac{1}{10}$ per cent potassium nitrate, a material improvement. I had feared to attempt titrating, with filter-paper suspended in the solution, but Mr. Handy's good results show that this fear was unfounded.

The reaction which takes place when the sodium hydrate solution is added to the yellow precipitate is an interesting study. I think that the yellow precipitate has the composition $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. I believe that the ammonia in this compound is replaced by soda when excess of sodium hydrate is added. I think that with the conditions of dilution which we operate under, the ammonia would be held in solution.

Mr. VAN GUNDY—I believe that the soda does not replace the ammonia; for, if it did, then an exactly equivalent amount of ammonia would be set free, and the alkalimetric value of the resultant solution would be identical with that of the measured amount of soda solution which was added. As practice shows that this is not the case, but, as the amount of soda used up varies with the amount of yellow precipitate present, I believe that the base of the soda unites directly with the phospho-molybdate of ammonia to form a neutral compound.

Mr. HANDY—I favour Mr. Van Gundy's theory.

Mr. MANBY—I believe that there is a certain amount of nitric acid which ordinarily separates out with the yellow precipitate, and is not removed by drying at 100° C., but is expelled by higher heat.

Mr. HANDY—My experience and study do not let me believe in the presence of nitric acid in the yellow precipitate, either (a) when washed with 1 per cent nitric acid

and dried at 100° C., or (b) when washed with 1 per cent nitric acid and then with $\frac{1}{10}$ per cent potassium nitrate, and not dried. I prepared pure yellow precipitate by washing with 1 per cent nitric acid and drying at 100° C. This material was placed in glass-stoppered bottles to prevent re-absorption of moisture. Portions of this yellow precipitate exposed for a half-hour to temperatures from 135° to 165° C. in an air-oven, no loss of weight was found in either case.

In regard to the presence of nitric acid in the yellow precipitate after washing with 1 per cent nitric acid, and then with $\frac{1}{10}$ per cent potassium nitrate, I do not believe in it for the reason that almost identical results are obtained by titrating by my process the undried and the dried precipitates. Slight variations were occasionally obtained, but I found a higher value for the dried than the undried precipitates. These two facts, I think, effectually disprove the presence of nitric acid in the yellow precipitate.

We have, further, the statement of Dr. F. Hundeshagen, in his most elaborate research (*Zeit. Anat. Chem.*, 1889), that the yellow precipitate obtained by precipitation under conditions which are the same that we have in our method, has the composition $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, when dried at 150°. No nitric acid is in the formula.

Mr. EASTWICK (to Mr. Manby)—Do you not consider the precaution of making your standard sodium hydrate solution free from carbonate of sodium a very necessary one?

Mr. MANBY—I do; and I give Mr. Handy credit for this good suggestion.

Mr. CARNAHAN—I have found slight loss of weight to take place when yellow precipitate, dried at 100° C., is exposed to a temperature of 150° C. The loss did not amount to more than 1 per cent of the weight of the yellow precipitate.

Mr. C. M. JOHNSON—I also have found a loss of weight when the yellow precipitate, dried on a filter at 100° C., is exposed to 150° C.

Mr. HANDY—I believe that Mr. Carnahan's and Mr. Johnson's losses of weight were due to the oxidation of the carbon of the filter at the expense of the oxygen of the molybdate. This action is evidenced by the progressive blueing of the filter and precipitate when exposed longer than three-quarters of an hour to a temperature of 100° C. or over.

My experiments were made by heating pure yellow precipitate in porcelain crucibles. I thus avoided any error caused by filter-paper oxidation.

PROCEEDINGS OF SOCIETIES.

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Address by ALBERT B. PRESCOTT, Retiring President,
Delivered at the Rochester Meeting, 1892.

(Concluded from p. 316).

WHAT I have said of the literature of one science can be said, in the main, of the literature of the other sciences. And other things ought to be said of what is wanted to make the literature of science more accessible to consulting readers. *A great deal of indexing is wanted.* Systematic bibliography, both of previous and of current literature, would add a third to the productive power of a large number of workers. It would promote common acquaintance with the original communications of research, and a general demand for the serial sets. Topical bibliographies are of great service. In this regard I desire to ask attention to the annual reports of the committee

on Indexing Chemical Literature, in this association for nine years past, as well to recent systematic undertakings in geology, and like movements in zoology and other sciences. Also to the Index Medicus, as a continuous bibliography of current professional literature.

Societies and institutions of science may well act as patrons to the bibliography of research, the importance of which has been recognised by the fathers of this Association. In 1855, Joseph Henry, then a past president of this body, memorialised the British Association for co-operation in bibliography, offering that aid of the Smithsonian Institution which has so often been afforded to publications of special service. The British Association appointed a committee, who reported in 1857, after which the undertaking was proposed to the Royal Society. The Royal Society made an appeal to Her Majesty's government, and obtained the necessary stipend. Such was the inception of the Royal Society Catalogue of Scientific Papers of this century, in eight quarto volumes, as issued in 1867 and 1877. Seriously curtailed from the generous plan of the committee who proposed it, limited to the single feature of an index of authors, it is nevertheless of great help in literary search. Before any list of papers, however, we must place a list of the serials that contain them, as registered by an active member of this Association, an instance of industry and critical judgment. I refer to the well known Catalogue of Scientific and Technical Periodicals, of about five thousand numbers, in publication from 1665 to 1882, together with the Catalogue of Chemical Periodicals by the same author.*

Allied to the much needed service in bibliography, is the service in compilation of the Constants of Nature. In the preface of his Dictionary of Solubilities, in 1856, Prof. Storer said "that chemical science itself might gain many advantages if all known facts regarding solubility were gathered from their widely scattered original sources into one special comprehensive work." That the time of the philosophical study of solution was near at hand has been verified by recent extended monographs on this subject. In like manner Thomas Carnelley in England, and early and repeatedly our own Prof. Clarke in the United States,† bringing multitudes of scattered results into co-ordination, have augmented the powers of chemical science.

What bibliography does for research, the Handwörterbuch does for education and for technology. It makes science wieldy to the student, the teacher, and the artisan. The chief dictionaries of science, those of encyclopedic scope, ought to be provided generally in public libraries, as well as in the libraries of all high schools.‡ The science classes in preparatory schools should make an acquaintance with scientific literature in this form. If scholars be assigned exercises which compel reference reading, they will gain a beginning of that accomplishment too often neglected, even in college, how to use books.

The library is a necessity of the laboratory. Indeed, there is much in common between what is called the laboratory method, and what might be called the library method, in college training. The educational laboratory was instituted by chemistry, first taking form under Liebig

* "Bolton's Catalogue of Scientific and Technical Periodicals" (1885, Smithsonian) omits the serials of the societies, as these are the subject of "Scudder's Catalogue of Scientific Serials" (1879, Harvard University). On the contrary, "Bolton's Catalogue of Chemical Periodicals" (1885, N. Y. Acad. Science) includes the publications of societies as well as other serials. Chemical technology is also represented in the last-named work.

† The service of compilation of this character is again indicated by this extract from Clarke's introduction to the first edition of his "Constants" (1873): "While engaged upon the study of some interesting points in theoretical chemistry, the compiler of the following tables had occasion to make frequent reference to the then existing lists of specific gravities. None of these, however, were complete enough. . . ."

‡ The statistics of school libraries in the United States are very meagre, the expenditures for them being included with that for apparatus. For libraries and apparatus of all common schools, both primary and secondary, the annual expenditure is set at \$97,048 dollars, which is about seven-tenths of one per cent of the total expenditure for these schools.

at Giessen only about fifty years ago. Experimental study has been adopted in one subject after another until, now, the "laboratory method" is advocated in language and literature, in philosophy and law. It is to be hoped that chemistry will not fall behind in the later applications of "the new education" in which she took so early a part.

The advancement of chemical science is not confined to discovery, nor to education, nor to economic use. All of those interests it should embrace. To disparage one of them is injurious to the others. Indeed, they ought to have equal support. It would be idle to inquire into their respective advantages. This much, however, is evident enough, chemical work is extensive, and there is immediate want of it.

Various other branches of science are held back by the delay of chemistry. Many of the material resources of the world wait upon its progress. In the century just before us the demands upon the chemist are to be much greater than they have been. All the interests of life are calling for better chemical information. Men are wanting the truth. The biologist on the one hand, and the geologist on the other, are shaming us with the interrogatories that ought to be answered. Philosophy lingers for the results of molecular inquiry. Moreover, the people are asking direct questions about the food they are to eat, or not to eat, asking more in a day than the analyst is able to answer in a month. The nutritive sources of bodily power are not safe, in the midst of the reckless activity of commerce, unless a chemical safeguard be kept, a guard who must the better prepare himself for his duty.

Now if the people at large can but gain a more true estimation of the bearing of chemical knowledge, and of the extent of the chemical undertaking, they will more liberally supply the sinews of thorough-going toil. It must be more widely understood that achievements of science, such as have already multiplied the hands of industry, do not come by chances of invention, nor by surprises of genius. It must be learned of these things that they come by breadth of study, by patience in experiment, and by the slow accumulations of numberless workers. And it must be made to appear that the downright labour of science actually depends upon means of daily subsistence. It must be brought home to men of affairs, that laboratories of seclusion with delicate apparatus, that libraries, such as bring all workers together in effect, that these really cost something in the same dollars by which the products of industrial science are measured. Statistics of chemical industry are often used to give point to the claims of science. For instance, it can be said that this country, not making enough chemical wood pulp, has paid over a million dollars a year for its importation. That Great Britain pays twelve million dollars a year for artificial fertilisers, from without. That coal tar is no longer counted a by-product, having risen in its value to a par with coal gas. But these instances, as striking as numerous others, still tend to divert attention from the more general service of chemistry as it should be known in all the economies of civilisation.

It is not for me to say what supplies are wanted for the work of chemists. These wants are stated, in quite definite terms, by a sufficient number of those who can speak for themselves. But if my voice could reach those who hold the supplies, I would plead a most considerate hearing of all chemical requisitions, and that a strong and generous policy may in all cases prevail in their behalf.

If any event of the year is able to compel the attention of the world to the interests of research, it must be the notable close of that life of fifty years of enlarged chemical labour, announced from Berlin a few months ago. When thirty years of age August Wilhelm von Hofmann, a native of Giessen and a pupil of Liebig, was called to work in London. Taking hold of the organic derivatives of ammonia, and presently adopting the new discoveries of Wurtz, he began those masterly contributions that

appear to have been so many distinct steps towards a chemistry of nitrogen, such as industry and agriculture and medicine have thriven upon. In 1850 he opened a memoir in the *Phil. Trans.* with these words: "The light now begins to dawn upon the chaos of collected facts." Since that time the coal tar industry has risen and matured, medicine has learned to measure the treatment of disease, and agriculture to estimate the fertility of the earth. It seems impossible that so late as March of the present year he was still sending his papers to the journals. If we could say something of what he has done, we could say nothing of what he has caused others to do. And yet, let it be heard in these United States, without such a generous policy of expenditure for science as gave to Dr. Hofmann his training in Giessen, or brought him to London in 1848, or built for him laboratories in Bonn and Berlin, without such *provision by the state*, the fruits of his service would have been lost to the world. Aye, and for want of a like broad and prudent provision for research with higher education, in this country, other men of great love for science and great power of investigation every year fail of their rightful career for the service of mankind.

For the prosecution of research, in the larger questions now before us, no training within the limitations of human life can be too broad or too deep. No provision of revenue, so far as of real use to science, can be too liberal. The truest investigation is the most prudent expenditure that can be made.

In respect to the support that is wanted for work in science, I have reason for speaking with confidence. If I go beyond the subject with which I began, I do not go beyond the warrant of the Association. This body has lately defined what its members may say, by creating a committee to receive endowments for the support of research.

There are men and women who have been so far rewarded that great means of progress are in their hands; to be vigorously held for the best advantage. Strength is required to use large means as well as to accumulate them. It is inevitable to wealth that it shall be put to some sort of use, for without investment it dies. By scattered investment wealth loses personal force. The American Association, in the conservative interests of learning, proposes certain effective investments in science. If it be not given to every plodding worker to be a promoter of discovery, such at all events is the privilege of wealth, under the authority of this Association. If it be not the good fortune of every investigator to reach knowledge that is new, there are, every year, in every section of this body, workers of whom it is clear that they would reach some discovery of merit, if only the means of work could be granted them. Whosoever supplies the means fairly deserves and will receive a share in the results. It is quite with justice that the name of Elizabeth Thompson, the first of the patrons, has been associated with some twenty-one modest determinations of merit recognised by this Association.

"To procure for the labours of scientific men increased facilities" is one of the constitutional objects of this body. It is time for effectiveness towards this object. The Association has established its character for sound judgment, for good working organisation, and for representative public interest. It has earned its responsibility as *the American trustee of undertakings in science*.

"To give a stronger . . . impulse . . . to scientific research" is another declaration of what we ought to do. To this end larger endowments are necessary. And it will be strange if some clear-seeing man or woman does not put ten thousand dollars, or some multiple of it, into the charge of this body for some searching experimental inquiry now waiting for the material aid. The committee upon endowment is ready for consultation upon all required details.

"To give . . . more systematic direction to scientific research" is likewise stated as one of our objects.

To this intent the organisation of sections affords opportunities not surpassed. The discussions upon scientific papers give rise to a concord of competent opinions as to the direction of immediate work. And arrangements providing in advance for the discussion of vital questions, as formally moved at the last meeting, will in one way or another point out to suitable persons such lines of labour as will indeed give systematic direction to research.

In conclusion, I may mention another, the most happy of the duties of the American Association. It is to give the hand of hospitable fellowship to the several societies who year by year gather with us upon the same ground. Comrades in labour and in refreshment, their efforts reinforce us, their faces brighten our way. May they join us more and more in the companionship that sweetens the severity of art. A meeting of good workers is a remembrance of pleasure, giving its zest to the aims of the year.

NOTICES OF BOOKS.

The Cry of the Children: an Essay in Tyranny and Ignorance. By A FREE LANCE.

OUR readers will doubtless remember that no very long time ago we had the pleasure of noticing a pamphlet by the present author on the "Organisation of Science." We find him now engaged in a task closely connected with the former,—a scathing exposure of education in general and of English education in particular. Its great sin is its still surviving classicism. True, other countries still compel boys and youths to waste precious time, and even more precious nerve-force, on dead languages. But in Britain alone are "nonsense verses" still kept up, and a correct knowledge of Latin and Greek prosody is held of more importance than a view into the laws of the cosmos. In fact, as the author clearly and fairly shows, the Englishmen who have gained the highest distinction in Science have done so not by dint, but rather in spite of, their training at school and university. What should we not accomplish were we not handicapped by the miserable pedantry which clings to us like a leprosy? Says A Free Lance, the book of Nature is for ever sealed: "because their teachers—save the mark!—disdained in their puny imbecility of ignorance to either know or teach aught of the laws and powers that animate this awful cosmos; sedulous alone to instil the genders of Latin nouns, the right pronunciation of Latin quantities, the genealogy of rascally scamps that never lived, the names of Trojan ships, the lewdness of mythic gods, and a thousand and one co-equal frivolities and trifles. These are thy gods, O Israel!"

As regards the choice of studies at schools and at colleges, he wisely condemns a hard and fast curriculum to be enforced upon all alike, irrespective of their varying powers and inclinations. He sums up this subject with the words, "let each do what he can best do, and all will best thrive." The adherence to classics he happily terms "a national foolometer."

That there is in this work much which we cannot accept, and more which does not fall within our jurisdiction, is undeniable. He will receive in many quarters censure which, if we rightly consider its utterers, must rank as the highest praise. Meantime, every voice raised against the old irrational system of education must be welcomed as an ally.

Process for Examining Commercial Spirits.—Ed. Mohler (*Annales de Chimie et de Physique*).—The author determines acids, ether, aldehyds, furfurol, homologous alcohols, and nitrogenous compounds, *i.e.*, ammonium salts, amides, pyridine bases, and alkaloids.

CORRESPONDENCE.

THE POSITION OF CHEMISTS.

To the Editor of the Chemical News.

SIR,—The letter of Mr. T. H. Davis, with its valuable suggestions, deserves the consideration of every chemist, and it is to be hoped that at last some effort will be made to properly organise what has become a valuable and indispensable profession. The time has gone by when the ordinary rule-of-thumb man held his own, and public bodies and private manufacturers have found that to be in any way successful and in a position to compete with our neighbours it is absolutely necessary to have the aid of science. It remains entirely with the profession whether it shall be paid adequately or not for its work and advice. But, on the other hand, if the public pay well for the services of a chemist it deserves some guarantee in return that he is competent and able to do his work, and a movement without including this will never be successful.

At present it is the exception for people to seek scientific advice except from a man known to have some special experience in the subject sought, and this should be a considerable help in the movement, as the majority of underpaid men are simply assistants or confine themselves to mere routine work. Make the terms on which a man enters the profession stricter, an examination in the particular branch he adopts necessary before he can take the post of chemist, and the result will be a gain to the profession and public.

I am quite aware that the Institute of Chemistry aimed at some such measures, but no chemist with any experience of technical work would consider that a Fellowship of the Institute was a guarantee that the bearer was competent to take the post of chemist to either a wet extraction works, or be consulted on a sewage scheme; neither am I aware that the public attach any more value to the F.I.C. than the F.C.S. From the large number of admissions of late years to the Chemical Society, the preference seems to lean to the latter. I fail to see what the Institute has done for analytical chemistry, and the sooner the profession turns its attention to an organisation by which they can be properly known to the public, the sooner will that end be reached which so many of us expected when the Institute was formed. I enclose my card and shall be very pleased to do all in my power to help forward any scheme for the advancement of the profession.—I am, &c.,

DARE LUCEM.

DISINFECTANTS—AN EXPLANATION.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, vol. lxxvi., p. 317, Mr. Wollheim, in answer to a letter of mine, which you kindly inserted in your issue of December 17th, explains what needs no explanation and omits to explain what is in want of explanation.

I had stated that aminol in the strength of one in six hundred does not kill the spores of anthrax in eight, nay, not even in twenty-four hours; it kills the sporeless *Bacillus anthracis*, the *Staphylococcus aureus*, &c., after prolonged exposure; one hour for sporeless *Bacillus anthracis*, two or more hours for *Staphylococcus aureus*, are practically prolonged exposure. These last statements Mr. Wollheim reiterates, without, however, mentioning the former, *i.e.*, the resistance of the spores.

Now, what Mr. Wollheim might have explained is this:—

1. Why does he call aminol of the strength of one in five thousand—that is the strength of the samples advertised—"a true disinfectant," knowing from my reports that such a strength, or one very near it, does not kill the *Staphylococcus aureus* in eight hours?

2. The leaflet on which my name is introduced in a seemingly misleading manner, and without my authority, and which accompanies the samples, gives in the form of a motto a quotation from Koch to the effect that no disinfectant can be called a true disinfectant that does not kill spores; yet, notwithstanding the fact that aminol even in the strength of one in six hundred fails to kill the spores of anthrax in twenty-four hours, the aminol solution of the strength of one in five thousand is described as "a true disinfectant."—I am, &c.,

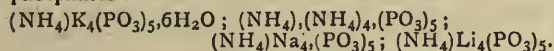
E. KLEIN.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

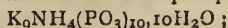
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal für Praktische Chemie.
New Series, Vol. xlv., Nos. 9, 10, 11.

A Contribution to our Knowledge of the Metaphosphates.—G. Tamman.—In concluding this extensive paper the author gives a conspectus of those series of metaphosphates the constitution of which is known to some degree, and an enumeration of those series the rational formulæ of which are still wanting. 1. Dimetaphosphates, $R'_2(PO_3)_2$. Trimetaphosphates of Fleitmann and Henneberg. 2. Trimetaphosphates, $R'_3(PO_3)_3$. Dimetaphosphates of Fleitmann. Both series of salts seem capable of containing members with all possible positive ions. There are further known numerous double salts of alkaline metaphosphates with metaphosphates of other metals. 3. Tetrametaphosphates. The only one known is Fleitmann's salt, $CuNa_2(PO_3)_4$. 4. Pentametaphosphates:—



5. Hexametaphosphates from Graham's soluble sodium metaphosphate, not crystalline; the sodium and silver salts are known; formula, $6R(PO_3)_6$. 6. Hexametaphosphates. The soluble potassium-sodium and lithium salts of the acid $2HNa_4(PO_3)_6$, and the two insoluble salts, $Ag_4K_2(PO_3)_6 \cdot H_2O$ and $3Sr_2K_2(PO_3)_6 \cdot 4H_2O$. 7. Octametaphosphates. By melting together magnesium-, cobalt-, nickel-, manganese- and zinc-sulphate with sodium metaphosphate; formula, $R'_8Na_2(PO_3)_8$. 8. Dekametaphosphates. Ammoniumdekametaphosphate,—



further the strontium, manganese, silver, and lead dekametaphosphates. 9. Tetrakaidemetaphosphates. A salt obtained by Gregory of the formula $Mg_6Na_2(PO_3)_{14}$. Series the formulæ of which are not yet determined:—1. The anhydrous insoluble copper, manganese, cobalt, and zinc metaphosphates. 2. The anhydrous insoluble lead, bismuth, barium, cadmium, and silver metaphosphates. 3 and 4. Two distinct insoluble sodium metaphosphates, one of which is crystalline. 5. The soluble crystalline potassium, sodium, and ammonium metaphosphates from vitreous metaphosphoric acid. 6. The salts insoluble in water, $(NH_4)_2Li(PO_3)_3 + 4aq$ and $K_2Li(PO_3)_3 + 2aq$. 7. A series of soluble metaphosphates of which the crystalline potassium salt has the composition $KPO_3 \cdot 3H_2O$. 8. A series of soluble, crystalline metaphosphates, of which $NaPO_3 \cdot H_2O$ and $3(KPO_3)_2H_2O$ are known.

Calorimetric Investigations.—F. Stohm.—Twenty-seventh Treatise.—This voluminous memoir is quite incapable of abstraction.

A Condensation Product of Benzaldehyd and Cyanacetic Ether: α -Cyancinnamic Ether.—J. T. Carrick.—In the formation of cyancinnamic ester it must be regarded as prominent that in proportion to the two

other substances in reaction small quantities of sodium ethylate are capable of effecting the condensation, which fails if the quantity of sodium ethylate is too large. Hence there is probably a formation of unstable intermediate products. The molecular weights of these compounds show that they are derivatives of cinnamic acid.

Contributions to the Chemistry of Manganese.—H. Schjerning.—The compounds here described are acid manganidpyrophosphate, $MnH.(P_2O_7)$, a violet coloured crystalline salt, insoluble in water, decomposed by acids and bases at ebullition. The author also describes the potassium manganidpyrophosphate, the manganidmetaphosphate, and the acid potassiumchromidpyrophosphate. He has also examined the sodiummanganometaphosphate and the behaviour of potassium permanganate with sodium sulphides.

Researches from the Laboratory of the University of Freiburg.—These comprise memoirs by G. N. Vis on ortho-oxethylanacetylamidquinoline; by P. Heermann on the $\alpha_1\alpha_2$ -amidonaphtholethylethers and some of their derivatives; by C. Willgerodt on the elaboration of dinitroazobenzol by F. Kehrman and J. Messinger; and by Ad. Claus, on Victor Meyer and the oximes.

No. 12.

The Naphthenes and their Derivatives in the General System of Organic Compounds.—W. Markownikoff.—The first portion of a treatise which does not admit of insertion on account of its extent.

The Constitution of Sodiumacetacetic Ether.—A. Michael.—An examination of the views of H. Neff on the constitution of this ether. Several of the experiments upon which Neff founds his conclusions are incorrect, e.g., the statement that aethylacetacetic ether is not reduced by sodium in an ethereal solution, whence the theoretical quantity of hydrogen is produced.

On Lavender Oil and Bergamotte Oil.—J. Bertram and H. Walbaum.—The authors assert that the English oil, so called Mitcham oil, meets with limited application on account of its high price. (They omit to add that the high price is a necessary consequence of its superior quality). The chief ingredient of the French lavender oil is an alcohol, $C_{10}H_{18}O$, and its esters, among which acetester predominates. The oil adds 4 atoms Br; with HCl it yields a liquid chloride, $C_{10}H_{18}Cl_2$, and by oxidation with chromic mixture it is converted into citral (gerenial), $C_{10}H_{16}O$. Dehydrating agents split off from the alcohol hydrocarbons, $C_{10}H_{16}$, among which terpenes and diterpenes can be distinctly traced. The alcohol is identical with the linalool of linaloe oil. The acetester of this compound is also found in oil of bergamotte.

On Aconitine.—Alex. Ehrenberg and O. Purfürst.—The authors remark that there exist at present six different empirical formulæ, of which that of Wright and Luff, $C_{33}H_{43}NO_{12}$, seems the most probable. That of Dunstan and Ince, $C_{33}H_{45}NO_{12}$, does not greatly differ. The authors prefer, however, the formula $C_{32}H_{43}NO_{11}$.

On Nitro- β -Naphtholes.—F. Gaess.—This paper does not admit of useful abstraction.

Bulletin de la Société Chimique de Paris.

Vols. vii. and viii., Nos. 20 and 21.

This number contains merely abstracts from other journals.

Revue Universelle des Mines et de la Metallurgie.
Series 5, Vol. xx., No. 1.

The only chemical matter here is a translation of a memoir by Frank Clowes presented to the Royal Society on the application of the safety lamp to the detection of vapours of benzene and other inflammable vapours diffused in the air.

MISCELLANEOUS.

Chicago Exhibition.—The World's Congress Auxiliary of the World's Columbian Exposition of 1893 (Department of Science and Philosophy: General Division of Chemistry) have issued the following Preliminary Address on a World's Congress of Chemists:—

It is proposed to hold a Congress of Chemists under the auspices of the World's Congress Auxiliary and the American Chemical Society, in Chicago, during the Columbian Exposition of 1893. The exact date of the Congress will be announced later, but it can now be said that it will be held after the middle of August, and at a time as near as possible to that at which other similar congresses will be held, in order to accommodate the greatest possible number of scientific men. While it is expected that a very general attendance of American chemists will be secured at this Congress, it is hoped that it may be honoured also by the presence of a large number of our foreign colleagues to take part in the discussion of topics from the various fields of theoretical and applied chemistry. During the Congress two classes of sessions will be held:—

a. International scientific meetings for the discussion of questions of interest to specialists. The programmes will be arranged by the Committees after they shall have received the advice and suggestions of persons interested. To these meetings all chemists and others working in scientific fields are invited.

b. Popular lectures on scientific topics of general interest, to be given by men of recognised prominence in the profession. It is expected that most of these lectures, which will be open to the general public, will be given by chemists from foreign countries.

For the convenience of specialists working in different fields it is proposed to divide the discussions of the scientific meetings into ten sections, as follows:—

1. Agricultural Chemistry.
2. Analytical Chemistry.
3. Didactic Chemistry.
4. Historical Chemistry and Bibliography.
5. Inorganic Chemistry.
6. Organic Chemistry.
7. Physical Chemistry.
8. Physiological Chemistry.
9. Sanitary Chemistry.
10. Technical Chemistry.

The World's Congress Auxiliary agrees to provide suitable halls for these scientific meetings as well as for the large popular gatherings. In this preliminary notice it is not intended to present more than an outline of what can be done, but later a more detailed statement will be made. As the members of an Advisory Council, from whom suggestions are solicited as to objects to be accomplished, topics for discussion, lectures on popular subjects, &c., the Committee gives a list of well-known American and foreign chemists. This list is not intended to be in any sense exhaustive or exclusive, and it is therefore hoped that all chemists interested in the success of the Congress will favour the Committee with suggestions regarding its work. From these suggestions it is expected that a general programme can be made up to be sent out at an early date.

Address all general replies or inquiries to J. H. Long, World's Congress Auxiliary, Chicago.

Special inquiries or suggestions relating to section work should be addressed as follows:—

In Agricultural Chemistry, to H. W. Wiley, Department of Agriculture, Washington, D.C.

In Analytical Chemistry, to A. B. Prescott, Michigan University, Ann Arbor, Mich.

In Didactic Chemistry, to P. T. Austen, 9, Cliff Street, New York, N.Y.

In Historical Chemistry and Bibliography, to H. C. Bolton, University Club, New York.

In Inorganic Chemistry, to F. W. Clarke, Geological Survey, Washington, D.C.

In Organic Chemistry, to I. Remsen, Johns Hopkins University, Baltimore, Maryland.

In Physical Chemistry, to R. B. Warder, Howard University, Washington, D.C.

In Physiological Chemistry, to V. C. Vaughan, Michigan University, Ann Arbor, Mich.

In Sanitary Chemistry, to H. Leffmann, 715, Walnut Street, Philadelphia, Pa.

In Technical Chemistry, to Wm. McMurtrie, 106, Wall Street, New York, N.Y.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 3rd.—Royal Institution, 3. "Astronomy," by Sir

Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

THURSDAY, 5th.—Royal Institution, 3. "Astronomy," by Sir

Robert S. Ball, M.A., D.Sc., LL.D., F.R.S.

FRIDAY, 6th.—Quckett Club, 8.

Geologists' Association, 8.

SATURDAY, 7th.—Royal Institution, 3. "Astronomy," by Sir Robert

S. Ball, M.A., D.Sc., LL.D., F.R.S.

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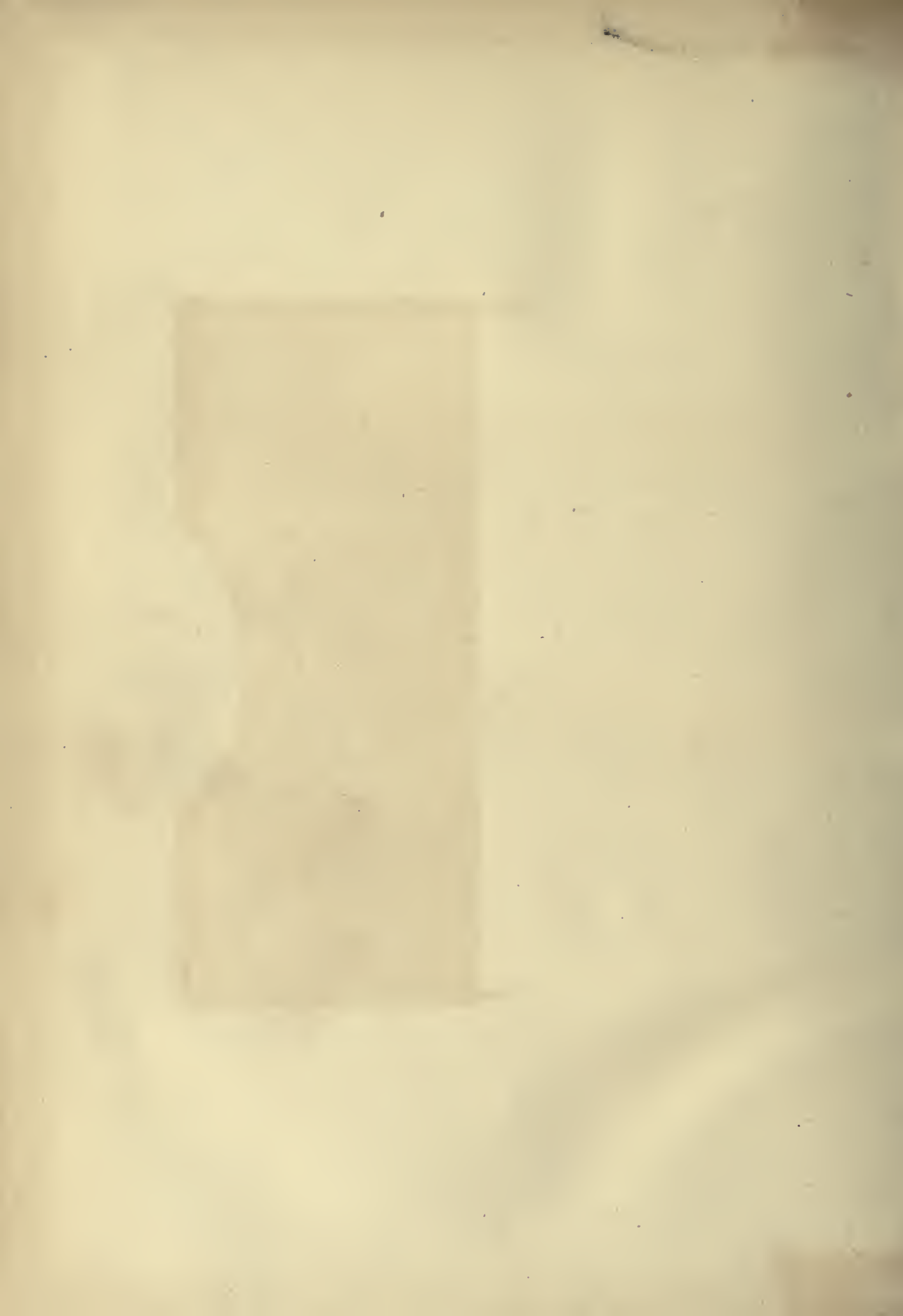
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ST. PAUL'S SCHOOL, West Kensington.—An Examination for filling up about four Vacancies on the Foundation will be held on the 18th January next.—For information apply to the Bursar, St. Paul's School, West Kensington.



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